Human impacts on the environment over the Holocene in Michigan and Illinois using lake sediment geochemistry

by

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David Philip Pompeani, PhD

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The legacy of human activity is recorded in natural archives such as ice cores and lake sediments. Together these reveal that humans have impacted the global carbon and metal cycles for thousands of years. However little is known about human-environmental change in the United States before European contact. This dissertation uses sorbed metals and stable isotopes of nitrogen measured in lake sediments to reconstruct past human-environmental change from two study regions: the Michigan Copper Districts and Cahokia (a Pre-Columbian city) near modern day East St. Louis, Illinois. Results from eight lakes suggest that distinct physical, geochemical, and isotopic changes associated with human impacts can be detected in lake sediments from the two study regions spanning from 9600 to 600 years before present (yr BP). These changes are consistent with the archeological record and occur at different times and magnitudes at each lake, indicating that the disturbances shifted through time. Sediments from seven lakes in the Michigan Copper District indicate that emissions from copper mining occurred from 9600 to 5000 yr BP when the archeological record suggests that hunter-gatherer societies known as the Old Copper Complex inhabited the region. Results from a lake near Cahokia in Illinois span the last ~1500 years when agricultural people lived in settlements and constructed earthen mounds along the Mississippi River. Sorbed metal concentrations and nitrogen isotope increases in the sediment after 1808 AD and from 1150 to 1350 AD. Changes after 1150 AD coincide with higher human populations during the height of Cahokia (i.e. Stirling and

Moorehead Phases) inferred from the archeological record. Overall, the data presented here provide a new window in which to document the responses of lake systems in the United States to human impacts in prehistory.

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PREFACE

It seems like a lifetime has passed since my journey at the University of Pittsburgh began. It was 2005 and I was 18 years old. The idea of pursuing a doctorate in geology had never crossed my mind. At that time just making it through my undergraduate degree seemed daunting enough. In my sophomore year, I took an introduction to geology course taught by Dr. Charlie Jones, and came to realize that being a geologist would be a worthy pursuit. I was always interested in the natural sciences as a child, acquiring microscopes, collecting insects, rocks, and with my Mom's support, various species of exotic pets. Without knowing it, I had learned much about freshwater lakes and geology while spending summers fishing with my friend Jeremiah Wade in the bay of Presque Isle, swimming in Lake Erie at Mike and Mary Lou Rathers' beach, hunting white tail deer with my Dad at my Uncle Rick's farm, and during family canoe trips each year on the Clarion River in Cooks Forest. The connection with earlier childhood interests that studying geology seemed to channel in my mind broke through the apathy for education that I had developed in my teenage years. After this realization, I no longer saw education as disconnected subjects, but rather as a way to becoming a better geologist!

After taking a class in sedimentology and paleoclimatology taught by Dr. Mark Abbott, the notion of pursuing a PhD first came to me. Dr. Abbott introduced me to paleolimnology – or the study of the evolution of lakes – using sediment cores. This new science had a lot of room to grow and could potentially be used to answer questions about the recent geologic history of the

world in ways that were not thought possible just decades ago. Eager to start research right away, I asked Dr. Abbott if I could work in his lab. I was hired in 2007 and that is when my life as a geologist began.

In 2008 I was part of a National Science Foundation (USA) funded research experience for undergraduates (REU) that travelled to Svalbard, an island archipelago north of Scandinavia in the Arctic. There, with Dr. Al Werner and Emily Mortazavi, I took my first sediment core from a lake named Linnévatnet. I analyzed the sediment core over the following year and presented the results at the 2009 Arctic Workshop at Bates College organized by Dr. Mike Retelle. That year I graduated with my undergraduate degree, and began to work for Dr. Abbott as a PhD student.

At first, using lakes to measure metal emissions from ancient copper mining in Michigan did not seem like a good idea to many of our colleagues. Dr. Abbott alone took the chance and supported my dissertation research. Similarly, Dr. Daniel Bain's support using the ICP-MS and his intensive review of the manuscripts produced with this data immeasurably improved this dissertation. In addition, countless hours spent talking with other graduate students – Byron Steinman, Aubrey Hillman, Matthew Finkenbinder, Christopher Purcell, and Alan Mur – contributed substantially to my growth as a scientist. Last but not least, I want to recognize Katherine Haas for her loving support at home and my family for always believing in me.

Funding for this dissertation came from Geological Society of America, grants and teaching fellowships through the Department of Geology and Planetary Science, a Mellon Predoctoral Fellowship, and instrumental support from the National Science Foundation.

1.0 INTRODUCTION

Human activities have shaped the environment for thousands of years and left a detectable signal in ice cores and lake sediment (Brenner et al., 2002; D'Anjou et al., 2012; Ruddiman, 2003; Ruddiman et al., 2011). Previous research has shown that Pre-Columbian societies (before 1492 AD) in North America shaped the landscape by altering vegetation (Beach et al., 2009; Mann, 2005; Munoz et al., 2014a; Rosenmeier et al., 2002). In addition, climate change appears to have coincided with both the development and disintegration of past societies (Hodell et al., 1995; Kennett et al., 2012; Meeks and Anderson, 2013). However, prior studies investigating the potential links between the Pre-Columbian societies and climate change attempt to compare archeological data with proxy drought reconstructions, such as tree rings, lake sediments, and speleothems (Benson et al., 2009; Hodell et al., 1995; Kennett et al., 2012; Meeks and Anderson, 2013). This approach is limited in its application, in part, because of the poor comparability between artifactual data and paleoclimate time-series. Overall, these studies suggest that both forces of nature, such as insolation and ocean-atmosphere dynamics that are traditionally incorporated into paleoclimate interpretations, and the growing impacts from humans, have shaped the Holocene landscape. However to date, little attention has been given to the potential for human alteration to affect proxy indicators obtained from lake sediments in the United States. Lake sediments are sensitive to human perturbations to the metal and nitrogen cycles in modern times. Therefore, sediment records that span the Holocene provide a window to document the responses of lake systems to human alteration of these cycles in the past. Using previously developed radiometric-dating techniques time-series of changing human activity are

developed using sediment cores from multiple lakes in the United States. The proxy data presented here provide a long-term perspective into the natural biogeochemical functioning of lakes and the response of those systems to both recent and prehistoric anthropogenic disturbances. This data will help to refine our understanding of how human activity impacts paleoclimate proxies such as fossil pollen or metals, which can then be compared to and refine interpretations of the archaeological record and our understanding of human-environmental relationships in the past.

This dissertation focused on two study areas: the Michigan Copper Districts on the Keweenaw Peninsula and Isle Royale, and Horseshoe Lake near Cahokia. These two study regions were selected because they contain suitable lakes for study, near regions where human activity was likely concentrated in the past. The copper using societies of the Lake Superior region are commonly referred to as the Old Copper Complex. The Old Copper Complex is a hunter-gatherer society radiocarbon dated to the Early and Middle Archaic periods from about 11500 to 5000 years before present (yr BP) (Martin, 1999). The copper sources exploited during the Old Copper Complex likely came from multiple deposits in North America, one of which is located in the Michigan Copper Districts. Lakes were cored near copper mines on the Keweenaw Peninsula and on Isle Royale to study how prehistoric copper mining from early hunter-gatherer societies in North America impacted the flux of metals lakes to infer the timing, magnitude, and processes by which human activities associated with the Old Copper Complex impacted the environment.

Cahokia, near modern day East St. Louis, Illinois is the largest known Pre-Columbian city in the United States (Pauketat and Emerson, 1997). It grew during the Late Woodland and Mississippian periods from about 1500 to 600 yr BP. Cahokia is one of the earliest urban

landscape (Iseminger, 2010; Pauketat, 2009) in the United States and the inhabitants relied on agriculture, including crops such as maize (*Zea Mays*) and beans (*Leguminosae*). Horseshoe is an oxbow lake located ~3 km north of Cahokia in a large, low relief floodplain situated on top of a shallow aquifer. I retrieved a core with 1500 years of sediments from Horseshoe Lake to investigate how earthen mound construction, agriculture, high population densities, and copper metalworking affected the lake.

By examining paleoenvironmental changes from different cultural periods that occurred in disparate regions in North America, I investigate how both hunter-gatherer and agricultural societies impacted the environment in ways that can be measured using the geochemical, isotopic, and physical composition of lake sediment. These changes appear to be distinct and vary in temporal and spatial scope. This data offers a new perspective for interpreting the human history of the Pre-Columbian United States and provide a window in which to analyze how lake ecosystems respond to past anthropogenic perturbations.

2.0 MICHIGAN COPPER DISTRICT

2.1 INTRODUCTION AND BACKGROUND

The copper deposits on the Keweenaw Peninsula and Isle Royale (Michigan, USA) are the largest source of native copper in North America (Rosemeyer, 2009) (Figure 2-1). Surveys of the region during the middle and late 19th century identified thousands of mine pits with widespread evidence of prehistoric human activity in the form of hammerstones and rock piles concentrated along the copper-bearing ridges found on the Keweenaw Peninsula and on Isle Royale (Hill, 1847; Whittlesey, 1862). Surveyors' excavating the prehistoric pits (Figure 2-2) uncovered large masses of worked native copper (Hagar, 1865; Lathrop, 1901), scaffolding (Wood, 1907), ladders (Whittlesey, 1863), and other mining tools (Foster and Whitney, 1850). Several accounts noted that abundant charcoal deposits surrounded the copper within the pits (Hagar, 1865; Holmes, 1901; Lathrop, 1901), suggesting prehistoric (or pre-European contact) people used fire to aid in extracting and processing the copper. Descriptions of the ancient mines indicate they had likely been abandoned for hundreds or thousands of years prior to their discovery (Gillman, 1880; Lathrop, 1901; Whittlesey, 1854). Although research has uncovered no evidence of prehistoric smelting around Lake Superior, it has demonstrated that prehistoric

North American peoples heated native copper with fire and worked (or annealed) the metal using rock hammers (Laronge, 2001; Martin, 1999).

Interest surrounding prehistoric mining and use of copper in North America has spawned over a century of research. Three copper-using traditions are recognized based on this work (Ehrhardt, 2009). The first of these traditions, commonly described as the Old Copper Complex (or Culture) occurred during the Middle Archaic (~7000 to 3700 years before present (yr BP)) and predates the regional appearance of ceramics and agriculture. Copper artifacts from this period are concentrated around the Upper Great Lakes and are characterized by the production of heavy copper-tool technology. Significant sites from this tradition include the Osceola and Oconto cemeteries in Wisconsin (Pleger and Stoltman, 2009). Later, in the Early Woodland (~2100 to 1500 yr BP), the Hopewell Exchange System (also called the Hopewell Tradition) developed and began to circulate exotic materials, including copper, across extensive trade networks in eastern North America (Ehrhardt, 2009). In particular, numerous ceremonial copper artifacts from this period were found within burial mounds located in the Ohio River Valley (Mills, 1922). By the Late Woodland (~1100 yr BP), the agricultural peoples of the Mississippian Tradition or Southeastern Ceremonial Complex predominated the social and political landscape across the Midwest and eastern North America until European contact in the 16th century (Pauketat, 2009). Copper artifacts from this period were recovered from excavations at the Spiro (Oklahoma) and Moundville (Alabama) archaeological sites, in addition to a copper workshop identified at archaeological sites of Cahokia (Illinois) (Kelly et al., 2009). In general, artifacts from the Old Copper Complex, the Hopewell and the Mississippian Traditions suggest considerable variability in the geologic source, production technique and use of copper (Ehrhardt, 2009; Levine, 2007).

Radiocarbon dates of organic matter found associated with copper artifacts indicate that people were using copper in the Upper Great Lakes region by ~9,000 to 7,000 years before present or 1950 AD (i.e. yr BP) (Beukens et al., 1992; Martin, 1993; Pleger, 2001). These dates suggest metal-use appeared earlier in North America than evidence currently found in Europe (Radivojević et al., 2010), Asia (Chiou-Peng, 2009) and South America (Aldenderfer et al., 2008). Further, the development of copper-working technologies in the Lake Superior region seemingly preceded agriculture and emerged during a time period that has traditionally been associated with hunter-gatherer societies (Martin, 1999; Pleger and Stoltman, 2009).

Here, I use lake sediment cores taken from eight lakes situated across the Michigan Copper District to reconstruct the timing, magnitude, and geographical pattern of copper mining pollution to make inferences about the ancient copper industry and the response to of lakes to anthropogenic disturbances. The Michigan Copper District contains numerous inland lakes with small catchments, situated in close proximity to known modern and prehistoric mining localities. Using comparable methodologies at each site I demonstrate that on a local scale, measurable levels of metalworking pollution were generated at discrete time intervals by ancient societies on the Keweenaw Peninsula starting as early as ~9,500 years ago.

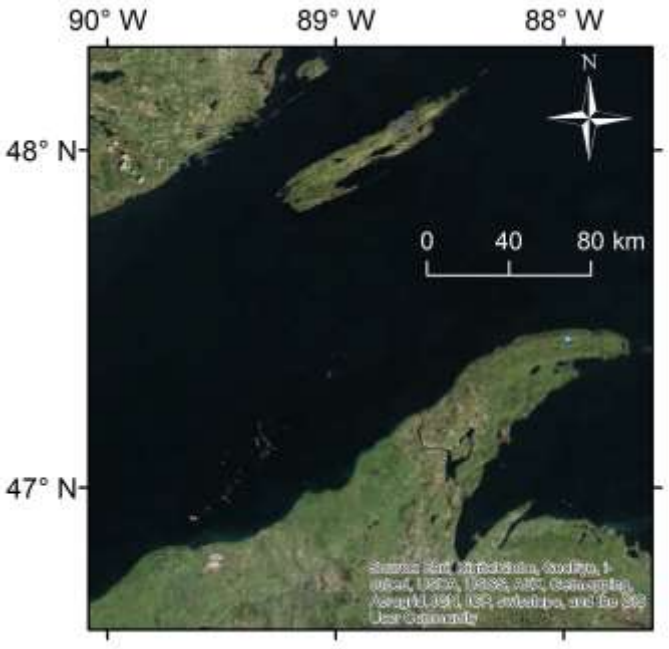
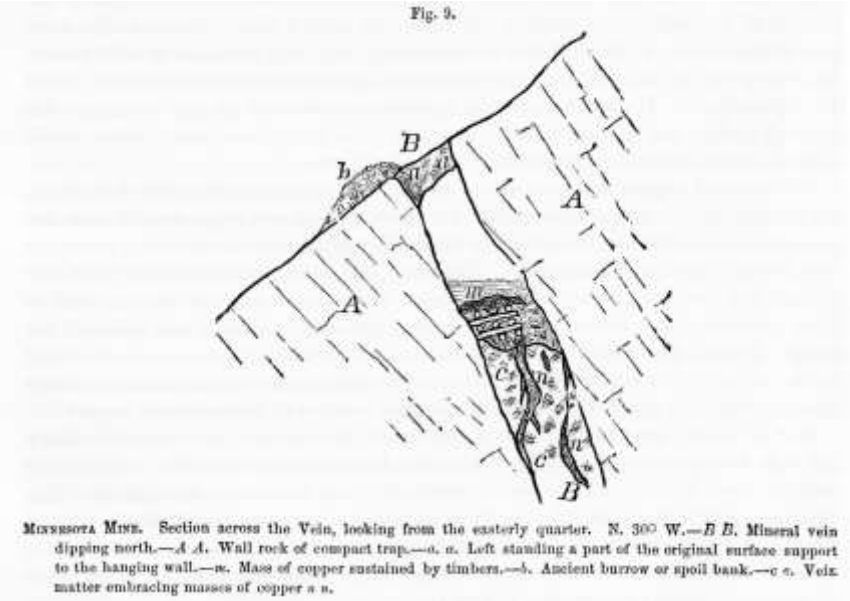


Figure 2-1 Aerial image of the Keweenaw Peninsula and Isle Royale in Lake Superior.

2.1.1 Historical evidence for ancient copper mining in Michigan

The earliest references to copper in the Great Lakes area comes from Jacques Cartier's second voyage in 1535-1536 AD. Cartier noted the presence of copper among the native peoples inhabiting the Gulf of St. Lawrence (Biggar, 1924; Griffin, 1961). In 1610 AD Samuel de Champlain met with Native Americans on the St. Lawrence River who offered him a bar of copper, that they said was from a source near a river draining into a large lake. For nearly 200 years following Cartier's and Champlain's accounts of copper, the French and British, with guidance from native groups, attempted copper mining in the southern Lake Superior region with limited success (Biggar, 1925; Lankton, 2010). Although native peoples guided Europeans to

pieces of float copper, there is no record of active copper mines (Whittlesey, 1863) or successful copper mining activity during the early European contact period with Native Americans (Griffin, 1961; Lankton, 2010). However, archeological evidence indicates that the indigenous peoples of the Upper Great Lakes used copper at the time of contact with Europeans (Martin, 1999).



Minnesota Mine. Section across the Vein, looking from the easterly quarter. N. 30° W.—*B B.* Mineral vein dipping north.—*A A.* Wall rock of compact trap.—*a. a.* Left standing a part of the original surface support to the hanging wall.—*n.* Mass of copper sustained by timbers.—*b.* Ancient burrow or spoil bank.—*c c.* Vein matter embracing masses of copper *n n.*

Figure 2-2 Cross-section image of a prehistoric copper mine from Whittlesey (1863).

In 1843 AD the Lake Superior Anishinaabeg (Ojibwe) peoples relinquished lands that included the Keweenaw Peninsula and Isle Royale, thus marking the beginning of modern copper prospecting in the region (Lankton, 2010). Accounts and maps drawn by Samuel Hill in 1847 AD provide some of the earliest written evidence for pre-contact copper mines on the Keweenaw Peninsula (Hill, 1847). Excavations of the pits, first reported by John Foster and Josiah Whitney in 1850 AD, confirmed that they were indeed produced by humans, and suggested that they were abandoned for centuries (Foster and Whitney, 1850). In 1862 AD, Michigan State Geologist Charles Whittlesey published a map (Figure 2-3) of the mines on the Keweenaw Peninsula (Whittlesey, 1862). This was followed by publications by Whittlesey

(1863) and Albert Hagar (1865), which further described the remains and attempted to obtain minimum ages for the mines by counting rings within tree stumps on top of the overburden piles (Hagar, 1865; Whittlesey, 1863). These tree ring counts suggested that the overburden piles were deposited several hundred years ago. Explorations at other copper districts around Lake Superior revealed even more extensive workings, such as Minong Ridge on Isle Royale (Gillman, 1873; Lane, 1900; Winchell, 1881).

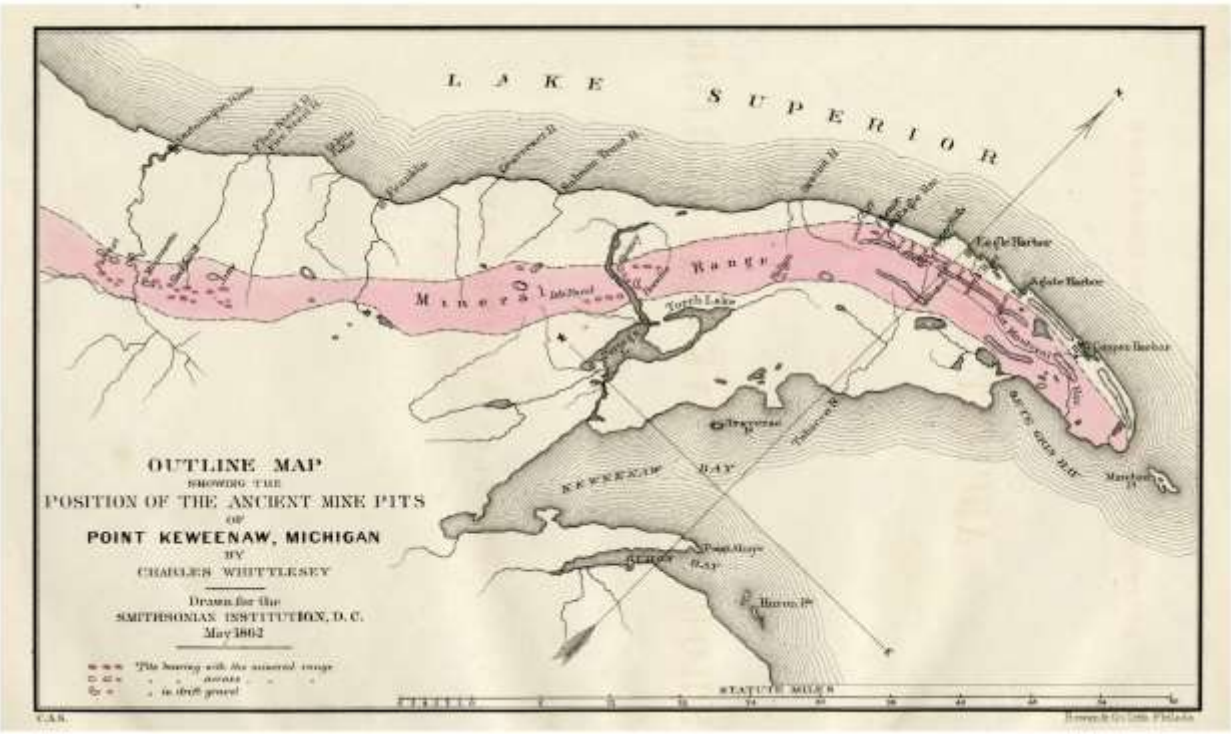


Figure 2-3 Outline map showing the position of the ancient mine pits of Point Keweenaw, Michigan from Whittlesey (1863).

2.1.2 Radiocarbon dating the Old Copper Complex

The advent of radiocarbon dating established the temporal context of copper-use around the Upper Great Lakes. Willard Libby was the first to radiocarbon date charcoal preserved with copper artifacts from Oconto archeological site. These analyses returned dates of 5600 ± 600 and 7510 ± 600 ^{14}C yr BP (or ~6400 and 8400 yr BP) (Libby, 1954). Subsequent radiocarbon dating of organic matter associated with copper artifacts confirmed the dates obtained by Libby (Binford, 1962 ; Mason and Mason, 1961). Additional work expanded the number of radiocarbon measurements by dating charcoal and wood preserved in copper pit mines on Isle Royale, extending the potential age range for copper mining to younger periods (Crane and Griffin, 1965).

The development of Accelerator Mass Spectrometry (AMS) radiocarbon dating made it possible to date smaller masses of organic macrofossils associated with copper. In the case of the Old Copper societies, native copper (a known bactericide and fungicide) helps to preserve organic matter. Beukens et al. (1992) were among the first to pioneer these techniques to date organic matter preserved with copper artifacts. The median calibrated AMS age of ~6800 yr BP (5940 ± 90 ^{14}C yr BP) from South Fowl Lake is still considered one of the oldest reliable dates for worked copper in North America (Beukens et al., 1992; Martin, 1999; Stuiver et al., 2010). More recently carbon preserved at the Oconto site, including a piece of string, has been dated using AMS radiocarbon methods with five ages spanning ~8400 to 5600 yr BP (Pleger, 2001). At Osceola, another prominent Old Copper site in Wisconsin, an estimated 500 individuals were buried in a grave pit with copper objects during a period younger than previously indicated by radiocarbon results. Two pieces of charcoal preserved in the grave pit were analyzed and had

ages of ~4600 and 3700 yr BP (4080 ± 70 and 3450 ± 250 ^{14}C yr BP) (Kuehn, 2002; Stoltman, 1997). In general, these and other radiocarbon analyses (Martin, 1993) indicate that copper use in the Upper Great Lakes region probably occurred over a period of several thousand years, beginning by the Early Archaic (~11500 to 6700 yr BP)(Pleger and Stoltman, 2009).

2.1.3 Geology of the Michigan Copper Districts

Indigenous peoples mined copper from open bedrock features such as trenches and pits, and heated the copper with wood fires (annealed) to aid in extraction and processing (Laronge, 2001; Martin, 1999; Schroeder and Ruhl, 1968). The Portage Lake Volcanic bedrock was targeted for mining because it contained large deposits of native copper "fissure veins" and vesicles containing secondary native copper (Rosemeyer, 2009). Copper mines and related piles of poor rock, tailings, and soil (i.e., overburden) occur frequently around Lake Superior where the PLV is exposed or near the surface. Poor rock contains low copper concentrations and was commonly piled near the mine entrance (or adit). Tailing refers to the remaining source rock and residues associated with the copper ore after processing (i.e. stamp mill, smelting, annealing, etc.). The occurrences of the mine pits were analyzed with respect to historical maps and modern geologic data in order to create a spatial algorithm for predicting the probable location of mine pits with respect to potential study lakes.

2.1.3.1 Midcontinental Rift

The copper-bearing rocks exposed on the Keweenaw Peninsula and Isle Royale are found along the northernmost portions of the Midcontinental Rift system, which extends 2000

kilometers from Kansas through the Upper Peninsula of Michigan where it turns eastward and ends in eastern Michigan. The Midcontinental Rift system traces it's origins to the Middle Proterozoic (~1090 million years ago or Ma) when the proto-North American Archean and Proterozoic terrains were dissecting by upwelling mantle plumes derived from mantle sources in the modern day Midwest and Upper Great Lakes region (Ojakangas et al., 2001a). Large volumes of basaltic magmas erupted and produced broad lava plateaus that were centered along a central rift axis. Further rifting formed a broad valley basin with multiple volcanic centers. Radiometric dating of the Midcontinental Rift basalts (i.e. Portage Lake Volcanic) using U-Pb in zircons suggests the deposition of the major basaltic flow occurred from approximately 1096.2 ± 1.8 to 1094.0 ± 1.5 Ma. The volcanoclastic Copper Harbor Conglomerate that was deposited stratigraphically above the Portage Lake Volcanic is dated to 1087.2 ± 1.6 Ma (Davis and Paces, 1990). This implies that erosion and deposition of the recently created volcanic terrain initiated soon after rifting created accumulation space. In combination this suggests that the eruption and formation of the Portage Lake Volcanic occurred over as little as 3 million years and was completed (marked by the deposition of the Copper Harbor Conglomerate) after approximately 10 million years (Ojakangas et al., 2001a).

Indirect evidence regarding mantle-plume dynamics across the Midcontinental Rift region can be obtained by studying the basalt flows associated with the Portage Lake Volcanics. The Portage Lake Volcanics are one of the largest basalt flows on earth and consist of eight volcanic centers or lava plateaus that are preserved in the rock record. The thickness of these units varies considerably from 0.1 to 6.0 km (Davis and Paces, 1990). In some instances, sedimentary units are interbedded within the lava flows therefore it is likely that periods existed following each basalt flow and which punctuated the transitions between the volcanic layers

(Ojakangas et al., 2001b). In addition, each flow was localized, which is consistent with multiple eruption centers. The lack of concentric volcanic centers suggests that the lavas erupted along fissures vents. Although mafic rocks predominate, volcanic units associated with the Midcontinental Rift vary considerably, and range from olivine tholeiite to rhyolite. Research suggests that the geochemical distribution of the lavas at the Midcontinental Rift is bimodal (i.e. either basalt or rhyolite). In many ways the geochemical variability of lava flows preserved in the rock record at the Midcontinental Rift mirror lavas in the East African Rift Valley region near the Afar Triple Junction. For example, the Yatta Basalt is the largest preserved flow on the East African Plateau and it marks a period of pronounced eruptions (i.e. from 13 to 11 Ma) during rift formation (Wichura et al., 2010). At the same time the Yatta was forming, similar phonolitic basalts erupted at the Afar Triple Junction indicating that rifting activity and similar lava flows extended across the region (Fruman et al., 2004; Wolfenden et al., 2004). In the both cases, the Midcontinental and the East African Rift basalts are typically high in Al content, similar to other plateau forming basalts. The low variability and generally mafic nature of the magma suggests deep mantle sources for the plumes (Ojakangas et al., 2001a).

2.1.3.2 Phanerozoic evolution of the Midcontinental Rift

The extensional forces that led to rifting failed after about 15 to 20 million years. Although the basins that formed from rifting are relatively diverse, their fundamental structure is the same. Each rift is defined by boundary of listric normal faults that are typically defined by asymmetrical grabens that follow the general trend of the rift. After rifting and volcanism had ended, sedimentation began which filled the Midcontinental Rift with up to 8 kilometers of clastic sediment. These sediments eventually led to the formation of the Copper Harbor

Conglomerate, Freda Sandstone, and the Nonesuch Shale. During later periods of sedimentation, the entire rift was covered the Jacobsville Sandstone (Cannon, 1992).

One hypothesis suggests that the extensional forces were generated by the early initiation of Grenville Orogeny to the east, which partially overlaps with the timing of rift development (Cannon, 1994). Regardless of the cause, the extensional forces appear to have been relatively short-lived. After post-rift cooling and sedimentation had ended, the basins were compressed and the normal faults were reactivated as high-angle reverse faults as the basins were uplifted potentially as a result of the Grenville Orogeny.

After rifting was aborted the region was geologically quiet for millions of years. During the Paleozoic Era (i.e. from 541 to 252 Ma), a large inland sea covered what is now the Michigan Basin. This sea deposited limestone and some dolomite rocks, which presently make up the Michigan Basin on the Lower Peninsula. During the Pleistocene Epoch (2.6 Ma to ~11700 yr BP) glaciations, the rocks deposited during the Paleozoic were eroded away to expose the copper-bearing Portage Lake Volcanics and Copper Harbor Conglomerate rocks (Cannon, 1994).

2.1.3.3 Predicting the location of the prehistoric copper mines using ArcGIS

In order to determine ideal study locations for lake pollution studies I identified probable localities for prehistoric mining. In this study I combine modern geospatial data with prehistoric mining locations from the Whittlesey (1862) map (Figure 2-3) in order to determine factors influencing the location of copper mines. By developing predictable relationships, I was able to identify lakes in close proximity to probable mine locations.

Early geological surveys of the region produced maps documenting the locations of prehistoric mining in the region (Whittlesey, 1862). Most early mining efforts centered on

ancient “indian diggings” as indicators for native copper loads because such little was known about in the geology of the Keweenaw Peninsula. Therefore, to evaluate the relationship between geospatial features (ex: topography, bedrock geology, surficial geology) of the peninsula (2002) and known prehistoric mining sites, the Charles Whittlesey mining map was georeferenced and projected into ArcGIS software (Whittlesey, 1862, 1863). Then, combinations of topographic, bedrock, and surficial geological features were tested against the historical maps of ancient copper mines to determine the probable location of prehistoric copper mining.

The occurrence of surficial outcrops of native copper is strongly influenced by bedrock geology. On the Keweenaw Peninsula several exposed bedrock types are known to bear native copper; the Portage Lake Volcanic metabasalts (Yplv), the Porcupine Lake Volcanic basalts (Ypv) and the Copper Harbor Conglomerate (Yc). Although each bedrock group bears native copper, each contains copper as various ores (sulfides, oxides) and in different forms, which may have been influenced exploitation by prehistoric miners. For example, *conglomerate* copper is found in sedimentary rock of the Copper Harbor Conglomerate, *amygdaloidal* copper derives its name from the Greek word meaning “almond” is found as secondary crystals in vesicular basalt, and *fissure* copper found as secondary crystals in veins and fractures in the Portage Lake Volcanic group (Lankton, 2010).

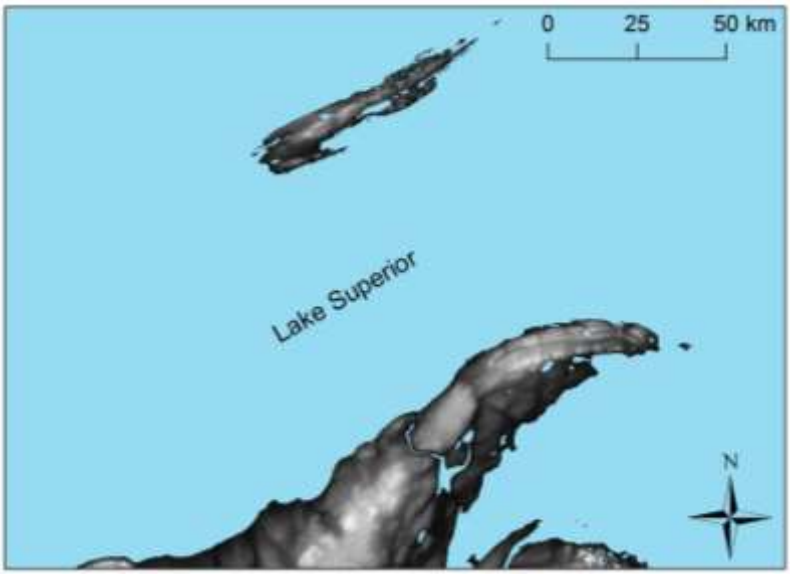


Figure 2-4 Digital elevation model (DEM) map of the Keweenaw Peninsula and Isle Royale. High elevation regions are in light grey.

The *fissure* copper of the Portage Lake Volcanic group formed the basis for the first profitable copper mines on the Keweenaw Peninsula in the middle to late 1800's (Rosemeyer, 2009). Most of the early historic mines used prehistoric mining evidence as an indicator of copper deposits, therefore from this suggests prehistoric miners exploited *fissure* copper deposits on the Keweenaw Peninsula (Lankton, 2010; Martin, 1999). These deposits would have been more ideal for prehistoric miners because they are found in bedrock resistant to erosion leading to the formation of topographically elevated ridges that have minimal Quaternary deposits covering them (Figure 2-4). In contrast to *amygdaloidal* and *conglomerate* native copper deposits which are more diffuse throughout the rock, the occurrence of additional deposits of copper in *fissure* vein deposits are easy to predict once discovered by following the strike and dip of the vein.

The access to copper *fissures* veins in the Portage Lake metabasalts was undoubtedly influenced by the thickness of surficial deposits that vary widely across the peninsula. These zones can be delineated and compared with the Whittlesey mines and bedrock geology map to investigate the relationship between surficial deposits, bedrock geology and documented copper mines. Under the effort minimization procurement model, prehistoric copper miners would have exploited areas of the Portage Lake Volcanics that were exposed at the surface and/or had thin discontinuous overlying surficial debris. These features were hollowed out on a surficial geology map and layered over a bedrock map to delineate regions with exposed bedrock at the surface (Figure 2-5). The intersecting layers areas can then be compared against the Whittlesey map to evaluate the relationship between the occurrence of mine pits and exposure of the Portage Lake Volcanic bedrock (Figure 2-6). The spatial comparison between the exposed Portage Lake Volcanic bedrock map with the Whittlesey map confirm the hypothesis that exposed areas of the Portage Lake Volcanic metabasalts were the likely sites of prehistoric copper mines.

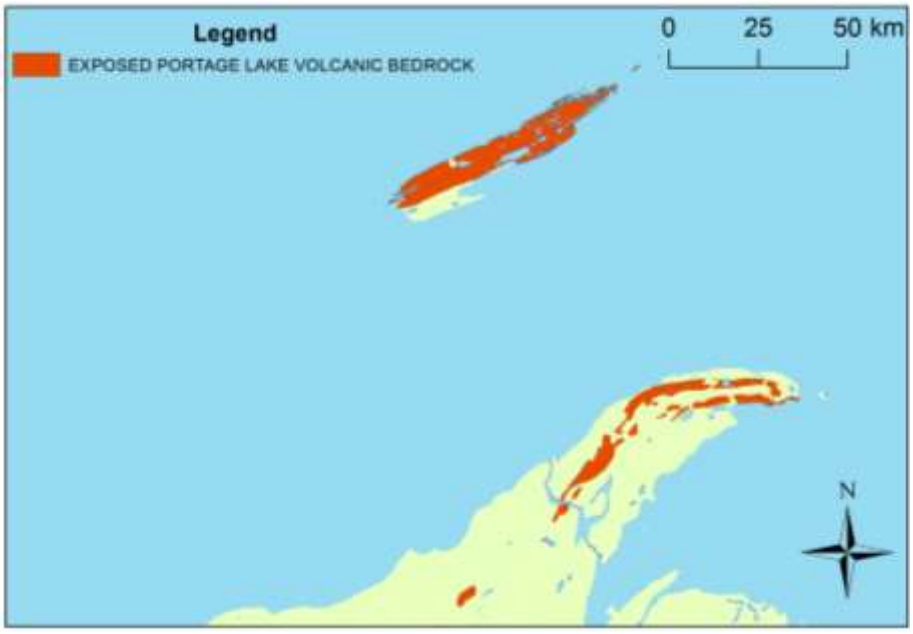


Figure 2-5 Map outlining the exposed regions of Portage Lake Volcanic bedrock on the Keweenaw Peninsula and Isle Royale.

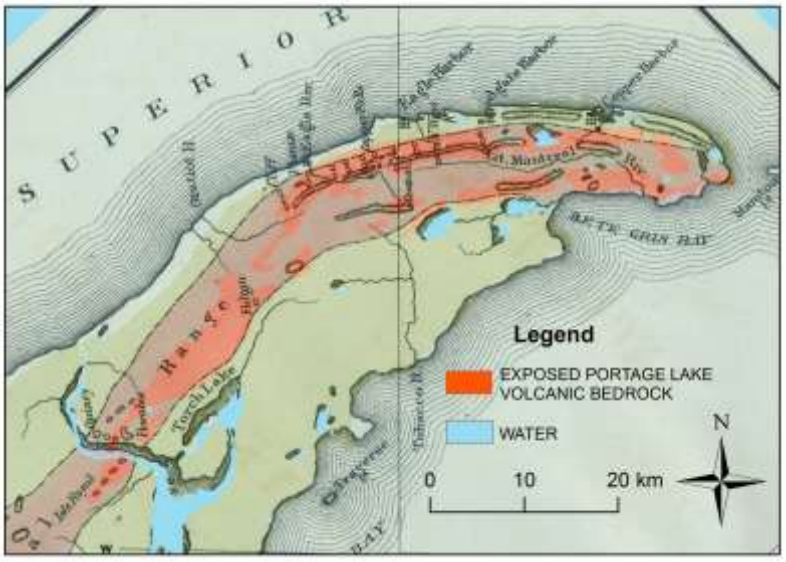


Figure 2-6 Exposed Portage Lake Volcanic bedrock in relation to mine mapped by Whittlesey (1862).

2.2 ISLE ROYALE RECONSTRUCTIONS

2.2.1 Introduction and background to McCargoe Cove and Chickenbone Lake

High densities of pre-contact (or prehistoric) mines are found along Minong Ridge on the northern shore of Isle Royale (Gillman, 1873; Lane, 1900; Winchell, 1881) (Figure 2-7). Excavations of these pits revealed depths up to 20 m and included tools such as rock hammers (i.e. hammerstones) and deposits of charcoal. Field surveys show that the mine pits are concentrated along a 3 km section of Minong Ridge starting from the western shoreline of McCargoe Cove (Gillman, 1873). The mining remains appear to be limited to the catchment of McCargoe Cove at Minong Ridge, located outside of the watershed of nearby Chickenbone Lake (Figure 2-8).

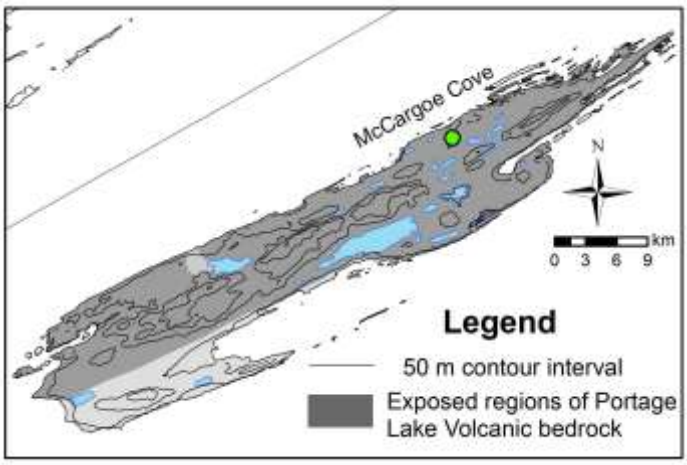


Figure 2-7 Isle Royale contour map with outlining exposed regions of the Portage Lake Volcanic bedrock.

Isle Royale is a freshwater archipelago comprised of a main island and approximately 200 smaller islands that stretch for ~70 km along the northwestern portion of Lake Superior. The copper-bearing Portage Lake Volcanic metabasalt bedrock formed topographic ridges that remained as islands in Lake Superior following deglaciation around 12000 yr BP (Clayton, 1983; Lewis and Anderson, 1989). The surface elevation of Lake Superior varied substantially following deglaciation (Lewis et al., 2008). The Nippissing, known as the highest lake-level transgression during the last 8000 years, peaked sometime between 5000 and 4500 yr BP (Blewett, 2009; Breckenridge, 2013) (Figure 2-8). After ~4000 yr BP water levels fell to near modern and remained there until today. Numerous inland lakes and wetlands separated by bedrock ridges that parallel a southwest-northeast trend are found on Isle Royale. January temperatures average -11° C, and July temperatures average 14° C with large temperature gradients between coastal and inland portions of the island (Flakne, 2003). Soils are poorly developed, especially on bedrock ridges, limiting vegetation cover. In areas with sufficient soil to support trees, such as around McCargoe Cove, boreal forests are present including species such as: white birch (*Betula papyrifera*), aspen (*Populus tremuloides*), balsam fir (*Abies balsamea*), white pine (*Pinus strobus*), white spruce (*Picea glauca*), sugar maple (*Acer saccharum)*, with occasional occurrences of red oak (*Quercus rubra*) (Flakne, 2003).

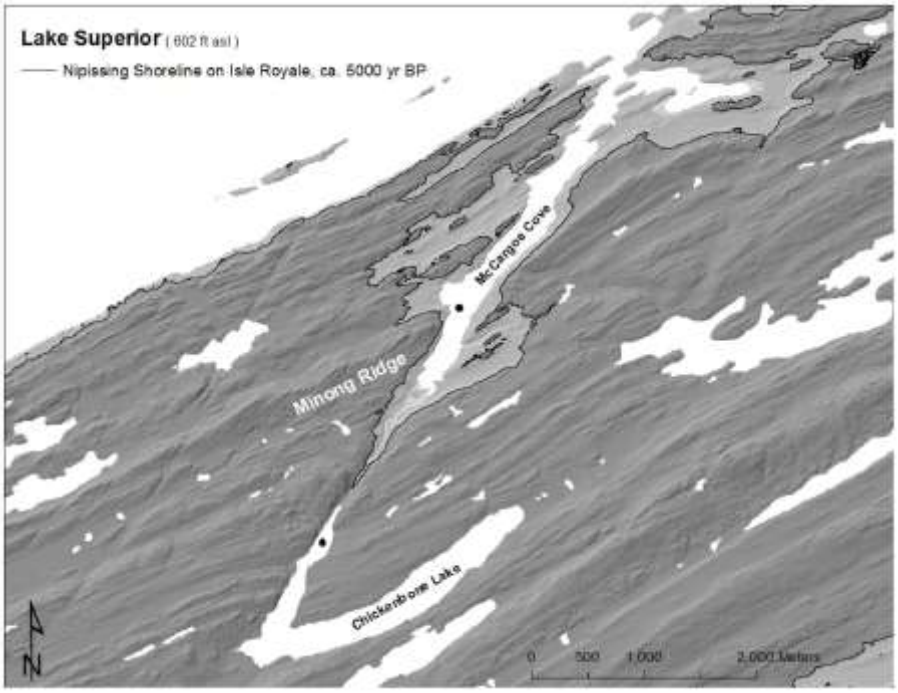


Figure 2-8 A LIDAR map of McCargoe Cove and Chickenbone Lake showing the modern shoreline of Lake Superior and the estimate shoreline from the Nipissing Highstand ~5000 yr BP.

The Portage Lake Volcanic bedrock was targeted for mining because it contains large deposits of native copper "fissure veins" and vesicles containing secondary native copper (2.1.3.3)(Rosemeyer, 2009). Copper mines and related piles of poor rock, tailings, and soil (i.e. overburden) are frequently found around Lake Superior where the Portage Lake Volcanic bedrock is exposed or near the surface. Poor rock contains low copper concentrations and is commonly piled near the mine entrance (or adit). Tailing refers to the remaining source rock and residues associated with the copper ore that remains after processing (i.e. stamp mill, smelting, annealing, etc.). Runoff from indigenous overburden piles and mine pits on Minong Ridge flows directly into McCargoe Cove, providing a unique location in which to measure past sedimentological and geochemical disturbances associated with pre-contact mining. Results from McCargoe Cove was compared with geochemical data from nearby Chickenbone Lake because

no substantial ancient mines or overburden piles are located in the catchment of therefore it serves as a control site to investigate the contrasting impact of mining at two sites on the Isle Royale.

2.2.1.1 Brief overview of Isle Royale archeology

Little is known about the Archaic period (~11500 to 2000 yr BP) on Isle Royale because most archaeological surveys focused on the present shoreline where precontact sites are limited to Woodland contexts (~2000 to 500 yr BP)(Clark, 1995, 1996). Archaic sites are restricted to the elevated beach ridges and the higher areas above them because the relative water level of Lake Superior has decreased since the Nippissing transgression (~5000 yr BP)(Figure 2-8). An Archaic human presence on Isle Royale is inferred from radiocarbon measurements on charcoal preserved at the bottom of prehistoric copper mine pits near McCargoe Cove (Crane and Griffin, 1965). However, little is known about the occupational and subsistence technologies used by Archaic societies on Isle Royale, in part, because no burials have been discovered that can be directly attributed to the prehistoric copper mining societies. Differences in hammerstone styles found on Isle Royale and the Keweenaw Peninsula have been noted (Martin, 1999). For example, Keweenaw Peninsula hammerstones usually show evidence of hafting (i.e. grooves carved into the rock for a strap wrapped around a handle)(Figure 2-9), whereas hammerstones on Isle Royale typically consist of a rounded igneous or metamorphic cobble with no evidence of hafting. Recent excavations on Isle Royale at the inland beach ridges do not reveal artifactual evidence typical of the Old Copper Complex (Clark, 1995), which is mainly found to the south of Lake Superior and typified by the copper-using cultures associated with human burials found at Oconto and Osceola Cemeteries in Wisconsin (Pleger and Stoltman, 2009). Radiocarbon

measurements associated with copper artifacts found north of Isle Royale at the Renshaw Site in Thunder Bay, Ontario and at South Fowl Lake in Minnesota reveal that they were produced in the Archaic period (Beukens et al., 1992). In summary, the artifact record from Isle Royale is sparse and current archaeological research indicates no outstanding connection between the Old Copper Complex material culture found in Wisconsin and Michigan beyond the use of copper technologies.

Figure 2-9 Prehistoric rock hammers from a locality near the former Delaware Mine on the Keweenaw Peninsula.

2.2.2 Methods

2.2.2.1 Fieldwork

In June 2012, five 1-m long overlapping Livingstone cores and a polycarbonate surface-sediment core spanning 3.6 m was taken at a water depth of 9.4 m in McCargoe Cove (48.0923° N, 88.7044° W, 2.3 km^2, 183 m asl) about 0.1 km northeast of Minong Ridge (Figure 2-8). Similarly, five 1-m Livingstone sediment cores and a polycarbonate surface-sediment core spanning 4.5 m were obtained in a water depth of 2.9 m in the northwestern tip of Chickenbone

Lake (48.0736° N, 88.7200° W, 2.0 km^2, 202 m asl). The sediment cores were wrapped in plastic wrap and sealed in ABS tubes for transport to the Department of Geology and Planetary Science at the University of Pittsburgh. The flocculate upper surface sediments were extruded in the field at 0.5-cm intervals to 30 cm depth and stored in Whirl-paks® for transport.

2.2.2.2 Radiometric dating

The age profile for the upper 20 cm of Chickenbone Lake and McCargoe Cove included ^{210}Pb assays, while the lower sections of cores were dated using AMS radiocarbon dates of terrestrial macrofossils. Radioisotope (^{210}Pb and ^{214}Pb) activities were interpreted using the constant rate of supply (CRS) model by direct gamma counting for 36 hours using a high-purity, broad-energy germanium detector (Canberra BE-3825) in the Department of Geology and Planetary Science at the University of Pittsburgh following a 3-week equilibration period in airtight petri dishes (Appleby and Oldfield, 1978; Binford, 1990; Lima et al., 2005). Sediment sub-samples extracted for radiocarbon dating were disaggregated with 7% H_2O_2 and sieved through a 125-µm screen to isolate terrestrial macrofossils. The macrofossils were picked using a small brush under a binocular microscope and were pretreated following standard acid-base-acid procedures (Abbott and Stafford, 1996). Radiocarbon samples were measured at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory.

2.2.2.3 Loss-on-ignition

In the laboratory, 1 cm^3 sub-samples were taken at 3-cm intervals down core from McCargoe Cove and at 5 cm intervals from the Chickenbone and dried at 60° C for 48 hours. Loss-on-ignition (LOI) was measured by combusting the dried sediments at 550° C for four hours and 1000° C for two hours to determine weight percent organic matter and carbonate content (Dean, 1974; Heiri et al., 2001).

2.2.2.4 X-ray diffraction analysis

The mineralogy of the McCargoe Cove sediment core was investigated by powder X-ray diffraction (XRD) using a Philips PW3710 X'Pert® X-ray Diffractometer at the University of Pittsburgh Swanson School of Engineering. Three 1-cm thick samples were taken at a mean depth of 51.5, 217.5, and 297.5 cm and pretreated using 7% H_2O_2 for 12 hours at room temperature to remove organic matter. The sediments were then washed with deionized water, frozen, lyophilized, and homogenized before XRD analyses. The spectra was analyzed using X'Pert Graphics and Identify® software to identify mineral assemblages present. No samples were analyzed from Chickenbone Lake.

2.2.2.5 Metal analyses and enrichment factor calculations

Sub-samples for metal analyses were taken at 3-cm intervals down the McCargoe Cove core and at 5-cm intervals down the Chickenbone Lake core. After preliminary analyses, one

interval of interest from each site was resampled continuously at 1-cm resolution down the McCargoe Cove core from 6500 to 5400 yr BP and from 9000 to 8100 yr BP at Chickenbone Lake. All the samples (n=192) were frozen, lyophilized, and homogenized and ~0.1 g of dry sediment was used for geochemical analyses. The metals were extracted by mixing homogenized dry sediment with 10% sub-boil distilled trace metal grade HNO_3 in 15 ml polypropylene tubes and constantly agitated at room temperature for twelve hours. Metals extracted from sediments using dilute HNO_3 are sensitive to inputs from human activities (Graney et al., 1995; Monna et al., 1999). Metal concentrations in the resulting supernatant were measured on a Perkin/Elmer NexION 300x Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at the Department of Geology and Planetary Science at the University of Pittsburgh. Detection limit is < 1 $\mu g\ g^{-1}$ for Pb, Cu, K, Ti, Mg, and Fe. Standards, blanks, and duplicates were measured during the analyses to ensure reproducibility.

Anthropogenic Pb enrichment factor indices were calculated using the methods in Shotyk et al. (1996), Weiss et al. (1999), and Boës et al. (2011). Multiple references (e.g. Ti, Fe, Mg, and organic matter) and site-specific average concentrations were used to produce four indices of Pb enrichments. The indices were then averaged to calculate a mean anthropogenic Pb enrichment factor (EF) with 95% confidence intervals. Background levels of Ti, Fe, Mg, and organic matter were estimated by taking the average of the entire record, whereas background (or natural) values for Pb, Cu, and K were calculated using the period from 5400 to 100 yr BP when there was minimal variation in metal concentrations. Spatial patterns of Pb input were determined by comparing the geochemical record from McCargoe Cove with those from lakes on the Keweenaw Peninsula.

At McCargoe Cove sediment archive sub-samples from one interval of interest from 6500 to 5400 yr BP were analyzed using an aqua regia extract to analyze mineral more strongly bound in the sediments. The sub-samples were crushed to a fine powder using an agate mortar and pestle. About 0.05 g of the crushed sediment was then placed in clean 7 ml Teflon reaction vessels with a screw on lid. The sediments were reacted with 4 ml of aqua regia consisting of a 3:1 mixture of concentrated sub-boiled distilled HCl and HNO_3 and placed on a hot plate at 80°C overnight with the lid lightly screwed on. The next day the caps were removed and the aqua regia mixture was evaporated off overnight under a fume hood. The next day the dried samples were then re-dissolved in 4 ml of 10% HNO_3 and the supernatant was extracted and measured for metals on the ICP-MS.

2.2.2.6 Portage Lake Volcanic bedrock analysis

Three small samples of rock from the surface of separate mine pits were obtained to characterize the metal composition of the bedrock surrounding the copper deposits on Minong Ridge. Samples were stored in labeled Whirlpaks® for transport. In the laboratory, the samples were washed with deionized water, dried and shipped to ALS Minerals for total metal analysis (procedure ME-MS41) (Table 2-5).

2.2.3 Results

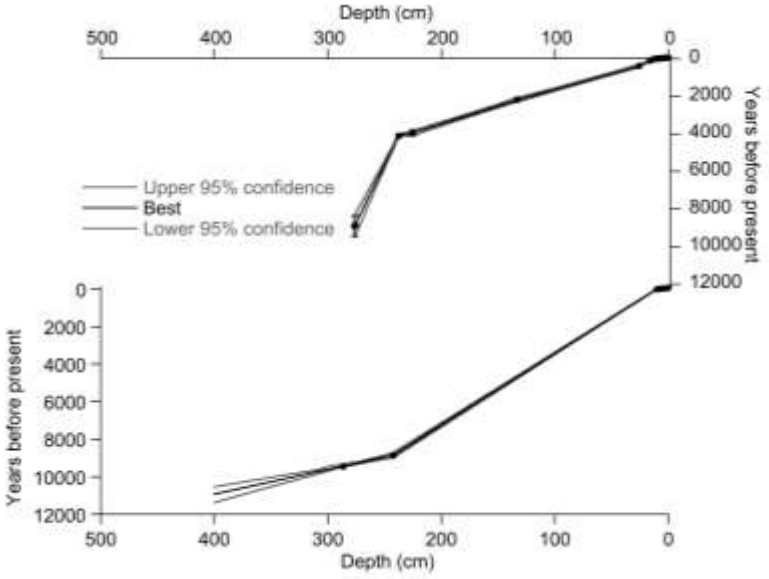


Figure 2-10 McCargoe Cove and Chickenbone Lake age-models.

2.2.3.1 Age models

A total of six radiocarbon and nine CRS ^{210}Pb dates were used to calculate an age-depth model for the McCargoe Cove core (Table 2-1). The Chickenbone Lake core was dated using a total of two radiocarbon dates and four CRS ^{210}Pb dates (Table 2-2). The ages were input into the CLAM package for R (Blaauw, 2010; Stuiver et al., 2010) to generate a linear point-to-point age-model and determine 95% confidence intervals for the interpolated ages (Figure 2-10). The dates from McCargoe Cove suggest that from ~8800 until 4000 yr BP, sedimentation rates in the cove were around 0.1 mm/year. From 4000 to -55 yr BP sedimentation rates increased to an average of 0.6 mm/year (Table 2-3). In Chickenbone Lake, dating resolution is limited

to two basal ages therefore sedimentation rates are poorly constrained (Table 2-4). Nonetheless, sedimentation rates are on average ~0.5 mm/year.

Table 2-1 McCargoe Cove Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP)	CRS Age (yr AD)	Error (1 sig)
0.25	0.323	0.034	0.278	-58	2008	1
2.25	0.356	0.037	0.584	-53	2003	1
4.25	0.332	0.035	0.952	-45	1995	2
6.25	0.314	0.033	1.293	-37	1987	2
8.25	0.296	0.031	1.745	-23	1973	2
10.25	0.214	0.023	2.216	-5	1955	3
12.25	0.118	0.015	2.727	14	1936	3
14.25	0.064	0.009	3.390	42	1908	5
16.25	0.037	0.005	4.119	104	1846	22
18.25	0.007	0.005	4.782			
20.25	0.000	0.000	5.515			

Table 2-2 Chickenbone Lake Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP)	CRS Age (yr AD)	Error (1 sig)
0.75	0.566	0.065	0.044	-60	2010	2
4.25	0.237	0.024	0.499	-46	1996	2
7.25	0.166	0.017	1.161	-21	1971	4
10.25	0.070	0.010	1.993	10	1940	7
13.25	0.031	0.006	3.161			
16.25	0.000	0.000	4.331			

Table 2-3 McCargoe Cove radiocarbon

UCIAMS #	Depth (cm)	^{14}C yr BP	Error (σ)	Calendar (yr BP[1])	Error (95% upper)	Error (95% lower)
116869	26.25	340	20	385	477	315
116870	133.50	2160	20	2162	2303	2066
122322	225.50	3640	60	3962	4148	3778
116871	237.50	3745	20	4112	4216	3992
116872	276.25	7980	260	8870	9484	8345
122323	276.75	8020	220	8907	9434	8424

[1]This is the median of the 95% calibration (CALIB 6.0) distribution (Stuiver et al., 2010).

Table 2-4 Chickenbone Lake radiocarbon

UCIAMS #	Depth (cm)	^{14}C yr BP	Error (σ)	Calendar (yr BP[1])	Error (95% upper)	Error (95% lower)
141374	242.50	7980	25	8874	8994	8726
141375	286.50	8410	25	9455	9494	9332

[1]This is the median of the 95% calibration (CALIB 6.0) distribution (Stuiver et al., 2010).

2.2.3.2 Visual sedimentology

The sediments in the McCargoe Cove core are red (Munsell color 5YR 5/2) from 360 to 260 cm and composed of minerogenic material with interbedded layers of sand. Above 260 cm (or ~7000 yr BP) the core transitions from red to brown (7.5YR 3/2) sediments with no sand layers present above this stratigraphic level. A transition occurs at 250 cm (~6000 yr BP) to a grey-colored (10YR 5/1) layer, which gradually changes to brown (7.5YR 3/2) sediments that remain from 245 to 0 cm (~5000 yr BP to present).

The sediments in the Chickenbone Lake core are red (Munsell color 5YR 5/2) from 440 to 230 cm and composed of minerogenic material with interbedded layers of sand. An abrupt

transition occurs at 256 cm (~9000 yr BP) to a grey-colored (10YR 5/1) layer, which gradually changes to brown (7.5YR 3/2) sediments that remain from 240 to 0 cm (~8800 yr BP to present).

2.2.3.3 X-ray diffraction data and organic matter concentrations

The detrital mineral content of McCargoe Cove sediment primarily consists of plagioclase series mineral assemblages. In particular, the three samples from depths 51.5, 217.5, and 297.5 cm (820, 5600, and >9000 yr BP [last age is extrapolated]) contain Na end-member plagioclase and alkali feldspar mineral matter ($CaAl_2Si_2O_8$, $NaAlSi_3O_8$, and $KAlSi_3O_8$). The McCargoe Cove core contains organic matter concentrations that are lower on average from 8800 to 4000 yr BP (~5%) and carbonate is below detection levels in the sediment. Organic matter gradually increases from 4000 to -55 yr BP reaching ~12% by weight. The Chickenbone Lake core contains ~3% organic matter concentrations on average from >10900 to 8600 yr BP (> indicates below last radiocarbon date). Organic matter concentrations are on higher on average from 8600 to -60 yr BP reaching an average ~20% by weight.

2.2.3.4 McCargoe Cove sorbed metal concentrations

Titanium (Ti), magnesium (Mg), and iron (Fe) concentrations remain at relatively stable average values of 85, 3150, and 9000 μg g^{-1} over the 8400-year record, with the exception of Mg, which was at higher concentrations (7000 μg g^{-1}) from 8400 to 6500 yr BP, and Fe, which increase to ~25000 μg g^{-1} after 0 yr BP (1950 AD)(Figure 2-11). From about 6500 yr BP to the

present, Ti, Mg, and Fe vary around their core average plus or minus two standard deviations (2σ) (Table 2-6).

Lead (Pb), Cu, and K concentrations are relatively high between 6500 to 5400 yr BP and 90 yr BP (1860 AD) to -55 yr BP (2005 AD). If these periods are omitted, sediment Pb, Cu, and K concentrations remain within their background average +/- 2σ. In sediments from 90 to -55 yr BP, Pb and Cu concentrations increase from ~ten- to three-times above background concentrations, whereas K does not increase above background levels. From 6500 to 5400 yr BP, Pb, Cu, and K concentrations rapidly increase to peaks of 14, 64, and 1140 μg g^{-1}, respectively, which is a ~seven-, two-, and six-fold increase above background values. Concentration changes of this magnitude are not recorded in Ti, Mg, Fe, and organic matter from 6500 to 5400 yr BP.

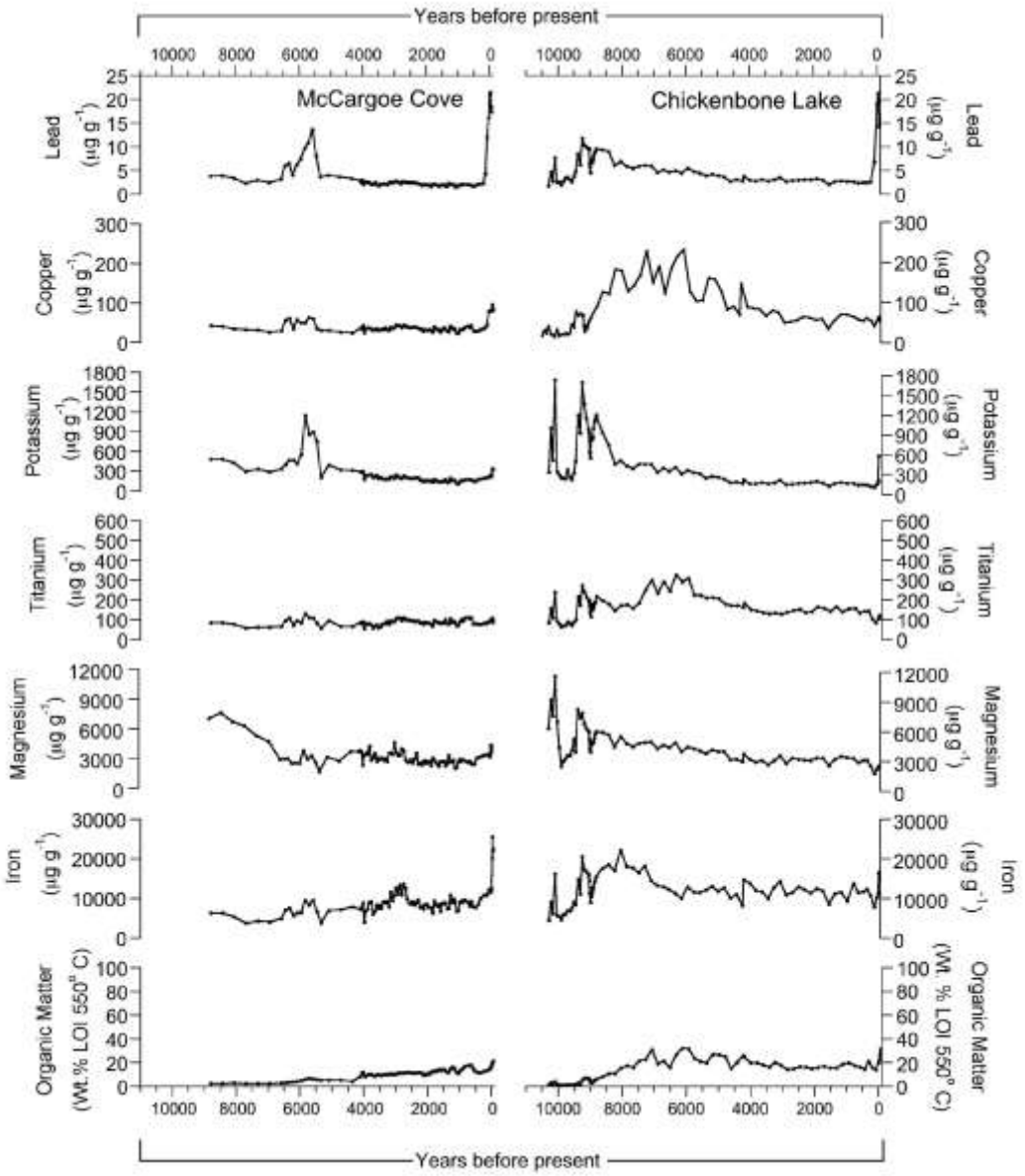


Figure 2-11 Sorbed metal concentrations and loss-on-ignition (LOI) results from McCargoe Cove and Chickenbone Lake.

2.2.3.5 Chickenbone Lake sorbed metal concentrations

Lead, K, Ti, Mg, and Fe concentrations are at relatively elevated concentrations of ~ 7, 900, 200, 6000, and 15000 μg g^{-1}, respectively from 10300 to 9000 yr BP (Figure 2-11). During the same time, Cu and organic matter concentrations are at low concentrations ~50 μg g^{-1} and 0% (Table 2-7). Starting 9000 yr BP organic matter begins to rise followed by Cu concentrations, which remain at elevated concentrations of ~150 μg g^{-1} from 8000 to 4000 yr BP. Around 8000 yr BP, Pb, K, Ti, Mg, and Fe concentrations all begin to decrease. Starting around 4000 yr BP the concentrations remained at stable and low values of 4, 250, 150, 3000 and 10000 μg g^{-1}. These values remained relatively constant until present, with the exception of Pb and K which rise to respective values of 21 μg g^{-1} in -30 yr BP (1980 AD) and 580 μg g^{-1} near the sediment water interface dated to -60 yr BP (2010 AD). The increase in Pb is more the five times greater than background concentrations observed for the last 6000 years and is higher than any other time since 10300 yr BP.

2.2.3.6 McCargoe Cove sediment aqua regia extractions

Archived sub-samples were digested in aqua regia to investigate metals strongly bound to the sediment over a period of interest 6500 to 5400 yr BP. The sub-samples (n=7) had an average concentration of ~10, 52, and 2660 μg g^{-1} for Pb, Cu and K, respectively, and average concentrations of ~2350, 11430, and 34300 μg g^{-1} for Ti, Mg, and Fe. Lead, Cu, K, Mg and Fe concentrations increase in the sediments, peak around 5600 yr BP, and decline in concentrations thereafter, whereas titanium concentrations decrease over the duration of this interval with minima centered ~5700 yr BP.

2.2.3.7 Portage Lake Volcanic bedrock metal concentrations at McCargoe Cove

Bedrock samples collected along the western shoreline of McCargoe Cove contained average concentrations of Pb, Cu, and K around ~10, 530, and 2,200 μg g^{-1}, respectively. Average Ti, Mg, and Fe concentrations were ~4,200, 12,800, and 44,700 μg g^{-1} (Table 2-5).

Table 2-5 Portage Lake Volcanic bedrock metal concentrations at Minong Ridge

Site #	Pb	Cu	K	Ti	Fe	Mg
2	9	455	2600	4590	41100	14200
3	9	967	2200	2430	31900	6300
6	11	171	1800	5660	61000	17800
Average[*]	10	531	2200	4227	44667	12767

[*]All values are in μg g^{-1}.

2.2.4 Discussions

2.2.4.1 Human influences on environmental metal cycling

Lake sediments record changes in metal inputs from the environment and human activities (Graney et al., 1995; Lee and Tallis, 1973; Renberg, 1986), as well as from recycling within the lacustrine system (e.g. redox)(Kalff, 2002). Lead, Cu, and K are used as proxies for mining and annealing activity occurring on Minong Ridge near McCargoe Cove. Two distinct periods of elevated Pb, Cu, and K inputs are recorded after 90 yr BP (1860 AD) and from 6500 to 5400 yr BP. If the periods associated with recent and Old Copper mining (i.e. 90 to -55 yr BP and 6500 to 5400 yr BP) are omitted from the analysis from McCargoe Cove, sediment Pb, Cu,

and K scatterplots with Ti, Mg, Fe, and organic matter cluster around a consistent range, referred to here as natural or background variability. Metal concentrations associated with human loadings plot outside the range of background variability (Figure 2-12) (Table 2-6).

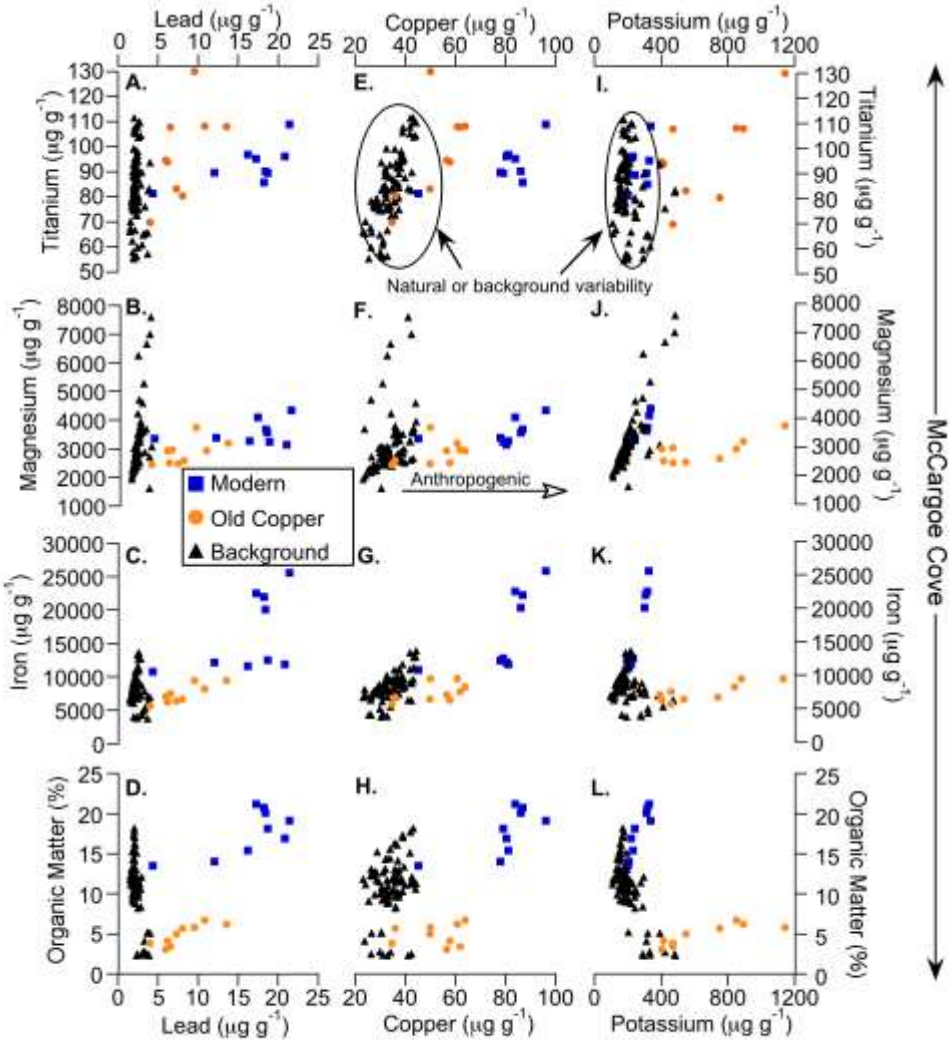


Figure 2-12 Scatterplot matrix of the proxy metal and organic matter concentrations (A-L) grouped into three time periods: Modern (90 to −55 yr BP), Old Copper (6500–5400 yr BP), and Background (8800–6500 yr BP and 5400–90 yr BP). Periods of human-related metal loadings at McCargoe Cove generally plot outside the range of natural or background variability.

Quantifying anthropogenic pollution requires accounting for inputs derived from a multitude of natural (or non-human) processes (Pacyna and Pacyna, 2001; Weiss et al., 1999). Chemical weathering in the catchment, along with contributions from the atmosphere are the primary natural sources of sorbed metals in lake sediments (Boyle, 2001; Cooke et al., 2007). To approximate these inputs, Pb was normalized to background references (Weiss et al., 1999). Four proxies (i.e. Ti, Mg, Fe, organic matter) were used for normalizing to capture the variety of natural processes distinctive to each lake (Boës et al., 2011). A 10% HNO_3 acid extraction method was utilized to isolate metals that are sorbed to organic matter, mineral surfaces and ferro-manganese oxides within the sediment (Graney et al., 1995; Shirahata et al., 1980; Tessier et al., 1979). Previous studies have demonstrated that concentrations of metals sorbed to sediment surfaces and liberated using weak acid extraction methods are sensitive to anthropogenic inputs (Abbott and Wolfe, 2003; Gobeil et al., 2013; Graney et al., 1995). In contrast, total digestions incorporate metals held within mineral lattices (Tessier et al., 1979), and consequently may reflect physical erosion rates in the catchment or other processes (Cohen, 2003) that could obscure an atmospheric signal (Boyle, 2001). Other environmental and geochemical controls within the lake (such as redox conditions in the water column) and catchment can substantially change the flux of sorbed metals over longer (e.g. millennial) timescales (Boyle, 2001). To account for this, iron (Fe) was used as a proxy for redox changes. Organic matter was used because metals often sorb to organic matter surfaces within the lake sediment, therefore variations down core could potentially influence metal concentrations (Boyle, 2001). Titanium (Ti) and magnesium (Mg) were used to approximate chemical weathering processes (Boës et al., 2011; Kerfoot and Robbins, 1999). Lead concentrations were applied to anthropogenic enrichment factor equations using Ti, Mg, Fe, and organic matter to

produce four indices of human-derived lead enrichment (Boës et al., 2011; Martinez-Cortizas et al., 2002; Weiss et al., 1999). All four indices were then averaged to produce a mean anthropogenic enrichment factor (with 95% confidence intervals), hereafter referred to as an EF. Anthropogenic EF values ≤ 1 are generally considered background levels.

2.2.4.2 Constraining natural variability

Organic matter concentrations are compared with the metal proxies because it provides sorption sites in the sediments and therefore changes in the amount of organic matter could affect metal concentrations in the sediments (Bloom, 1981; Bowen, 1979). Lower organic matter concentrations from early in both records suggest lower productivity in the early Holocene (Figure 2-11). After ~8000 yr BP at Chickenbone Lake and ~4000 yr BP at McCargoe Cove, organic matter concentrations rise, reflecting greater production and/or preservation of organic matter.

Changing concentrations of Ti, Mg, and Fe in McCargoe Cove and Chickenbone Lake sediments are interpreted to reflect shifts in the relative importance of processes influencing the delivery of metals to the basin, because these elements are found in high concentrations in the bedrock in the area (Table 2-5). For example, Ti concentrations are correlated changes in organic matter concentrations at both McCargoe Cove ($r^2 = 0.13$) and Chickenbone Lake ($r^2 = 0.18$), therefore are interpreted to reflect changes in soil erosion (Figure 2-11). Magnesium concentrations in the sediments are at relatively high concentrations prior to 6000 yr BP when organic matter concentrations are low. Increasing organic matter at both lakes corresponds with lower Mg, indicating either a dilution effect or a reduction of Mg delivered to the McCargoe Cove and Chickenbone Lake. Iron concentrations remain relatively unchanged in both records

reflecting stable redox conditions and/or Fe input to both sites over the duration of their records. In conclusion, Ti, Mg, Fe, and organic matter concentrations were used to account for a multitude of processes that influence the fluxes and preservation of metals in the sediments of McCargoe Cove and Chickenbone Lake.

Understanding the influence of natural sources of metals to lake systems is critical for estimating the influence of human-activities on atmospheric metal/metalloid cycles. The principal sources of natural atmospheric metals are wind-blown soil particles, volcanoes, seasalt spray and forest fires. Research suggests that about 50% of global metal emissions are of natural origin (Nriagu, 1989; Pacyna and Pacyna, 2001). However, for economically important metals such as Pb, the natural fluxes are much smaller than emissions from human activities. Today, about 9% of total global Pb emissions can be attributed to non-human processes, such as volcanic emanations and wind-blown soil particulates (Nriagu, 1989; Pacyna and Pacyna, 2001). Accordingly, we assume that in the absence of anthropogenic Pb emissions, dissolved fluxes from chemical weathering processes were the predominate Pb inputs to the study sites and that natural atmospheric Pb deposition contributed an insignificant Pb flux to lake sediments on the Keweenaw Peninsula.

Measurements of metal concentrations from a diversity of locations provide evidence for the occurrence of Pb pollution over the past 3000 years (Bindler, 2011; Nriagu, 1996). Recent lead contamination in the environment was first recognized by Patterson and colleagues (Patterson, 1965). Subsequent efforts using lake sediment cores, first by Lee and Tallis (1973) and later by Renberg (1986), documented the relationship between heavy metal contamination in lake sediments and smelting in Europe. Ice core reconstructions from Greenland confirmed these sediment based results, and further have demonstrated that pollution from early Greek and

Roman metallurgy was distributed throughout the northern hemisphere (Hong et al., 1994; Rosman et al., 1997). The use of sediment cores to document pollution chronologies has since expanded to other regions (Cooke et al., 2007; Zhao et al., 2011). For example, lake sediments recovered near ancient copper mining sites in the Hubei province of China record over 2000 years of Pb pollution (Lee et al., 2008), and in South America sediment records have been widely applied to understand the timing, magnitude, and technological evolution of mining and metallurgy over the past ~3000 years (Abbott and Wolfe, 2003; Cooke et al., 2008; Cooke et al., 2007). Collectively, these records and others have confirmed that preindustrial mining and metallurgical activities can leave a lasting environmental legacy preserved within natural archives.

Three reference elements (Ti, Mg, Fe) with varying geochemical properties and % organic matter were used to identify anthropogenic Pb variability relative to basin-specific background Pb delivery at McCargoe Cove and Chickenbone Lake. Site-specific reference or background values were calculated using the average of the entire record or in the case of the anthropogenic proxies Pb, K and Cu, the background average value was taken from 5000 to 100 yr BP (when human influences appear to be minimal. Metals (e.g. Ti) and organic matter do not necessarily covary within and between both the McCargoe Cove and Chickenbone Lake core sites. This lack of covariance implies that inter- and intra-site disparity in the lake settings (e.g. differences in hydrology, productivity and bedrock composition) influence changes in background metals and organic matter concentrations (Figure 2-11).

Table 2-6 Background values for McCargoe Cove core

Proxy	Average ($\mu g\ g^{-1}$)	Standard Deviation ($\mu g\ g^{-1}$)
Pb	2	1
Cu	34	5
K	189	49
Ti	85	15
Mg	3147	970
Fe	8972	3431
Organic matter	11*	4*

*Value is in percent.

Table 2-7 Background values for Chickenbone Lake core

Proxy	Average ($\mu g\ g^{-1}$)	Standard Deviation ($\mu g\ g^{-1}$)
Pb	5	2
Cu	77	52
K	475	381
Ti	164	58
Mg	4401	1664
Fe	12070	3550
Organic matter	13*	9*

*Value is in percent.

2.2.4.3 Proxies of human activities

Increases in Pb and Cu concentrations in the sediments from 90 to -55 yr BP (1870 to 2005 AD) are likely the result of the use of leaded gasoline and recent mining/smelting activities (Kerfoot and Robbins, 1999; Nriagu, 1996; Vermillion et al., 2005). Lead, Cu, and K concentrations increase above the range of background variability from 6500 to 5400 yr BP corresponding with several radiocarbon dates associated with copper artifacts found in the region (Beukens et al., 1992; Libby, 1954; Pleger, 2001) and Pb enrichment factor increases identified in lake sediments from the Keweenaw Peninsula. Due to our limited understanding of the

activities associated with ancient copper mining, I can only speculate as to the pathways in which metals were delivered to the sediment.

After 90 yr BP (1860 AD), copper inputs were probably related to some combination of leaching from rock debris and disturbed soils (transport enhanced by association with organic ligands), and/or atmospheric inputs from ore processing and/or smelting (Figure 2-11). Therefore, I assume increases in Cu concentrations from 6500 to 5400 yr BP also resulted from some combination of leaching and/or atmospheric inputs (e.g., annealing and wood burning). For example, annealing and hammering of native copper produces copper oxides (Peterson, 2003). In addition, numerous overburden piles were deposited on the surface of Minong Ridge, providing a potential source of dissolved copper to the McCargoe Cove. The limited understanding of Old Copper mining techniques, and the wide variety of minerals associated with native copper ore, make it difficult to predict emissions and leaching of metals in the past. Nonetheless I assume that increases in Cu concentrations after 90 yr BP and from 6500 to 5400 yr BP resulted from some combination of processes related to copper mining.

Interestingly, potassium (K) concentrations increase to 1140 $\mu g\ g^{-1}$ around 5800 yr BP. The lack of an increase in K concentrations during the historic mining period suggests that K is insensitive to deforestation and leachate from overburden recently deposited in the catchment (Holmes, 1892). Thus, a plausible mechanism must be invoked to explain the increase in K concentrations from 6500 to 5400 yr BP (Figure 2-11). Burning biomass, including wood, has been observed to preferentially release K (Calloway et al., 1989; Fine et al., 2001; Harrison et al., 2012; Kleeman et al., 1999; Larson and Koenig, 1994; Song et al., 2005) and produce water soluble potash (i.e. KOH). Potassium has also been used to infer biomass burning in ice cores (Eichler et al., 2011; Kehrwald et al., 2012). Therefore, I propose that K increases at McCargoe

Cove during Old Copper mining were likely related to some combination of inputs from wood fires (e.g. potash and wood smoke) and/or unknown processes related to ancient mining and annealing techniques.

The lack of an increase in K concentration in historic sediments raises questions about the differences between modern and Old Copper mining techniques (Figure 2-12). For example, the lack of a modern increase in K concentration in the sediments can be attributed to the relatively short duration of recent copper mining (i.e. from 1875 to 1885 AD) and low human populations relative to the apparent length Old Copper mining period (i.e. ~900 years). Or perhaps higher K concentrations resulted from forest fires, which emit K aerosols (Pio et al., 2008). However, these episodic events cannot explain the duration of the sustained K enrichment (~600 years) during the Old Copper mining period because the impacts of forest fires are short (< 1 year) and there are no K concentration increases in the sediments deposited during recent forest fires (Figure 2-11)(NPS, 2004).

In recent times, sources of Pb to the sediment were the result of inputs from regional and global Pb emissions (Pacyna and Pacyna, 2001), in part from burning fossil fuels and smelting, along with possible contributions from leaching recently deposited overburden piles in the catchment (Table 2-5). During the Old Copper mining period, Pb compounds could have come from overburden leachate or particulates volatized from fire associated with mining and annealing. Rising Pb concentrations from 6500 to 5400 yr BP contrasts with modern Pb pollution in that it is associated with higher concentrations of K (Figure 2-12), which is insensitive to inputs from overburden leachate. The association with higher K concentrations suggests that the source of Pb from 6500 to 5400 yr BP was derived from some combination of wood burning and/or unknown processes related to mining and annealing.

Lead, Cu, and K concentration follow unique trends during the Old Copper mining period. For example, maximum Cu and K concentrations occur ~5800 (+/- 200) yr BP, while Pb peaks ~5600 (+/- 200) yr BP (Figure 2-11). The observed lag in higher metal concentrations might be explained by changes in the nature and/or location of metalworking activities (i.e. technologies, ore composition (Table 2-5), and/or extraction rates) that influenced the relative fluxes of Pb, Cu, and K to the core site. However, this needs to be tested with additional proxies and archaeological data. Alternatively, the lag in the timing of peak Pb concentrations relative to the peak in Cu and K concentrations could be explained by the longer residence time of Pb in soils (Bowen, 1979). This does not appear to be consistent with the data, because Cu concentrations had doubled relative to background average values by 6300 yr BP, while Pb concentrations had tripled, and K remained near background levels. In general, the increases in Pb, Cu, and K concentrations produced by human activities far exceed background variability, providing a useful way to differentiate anthropogenic and natural metal inputs (Figure 2-12).

Lead concentrations abruptly increase in the sediments of Chickenbone Lake from 90 to -55 yr BP (1870 to 2005 AD), likely as the result of the use of leaded gasoline and recent mining/smelting activities (Kerfoot and Robbins, 1999; Nriagu, 1996; Vermillion et al., 2005). However, unlike McCargoe Cove, Cu concentrations do not increase in modern sediments and K concentration record minor increases at the sediment-water interface. The lack of a Cu spike in the recent sediments is expected because no modern mining occurred in the catchment and the lake is located in a remote part of the Michigan Copper Districts away from smelters. Higher Pb and K concentrations are limited to before 8000 yr BP is associated with higher concentrations of Ti, Mg, and Fe, therefore probably reflects higher erosion and chemical weather rates of bedrock following deglaciation. However, Cu concentrations closely follow trends in organic matter

(r^2=0.53) because it probably delivered to the lake bound to exchanges in terrestrial organic matter delivered to the lake.

2.2.4.4 Anthropogenic enrichment factors

Sorbed lead concentrations at both sites were normalized to three reference metals (Ti, Fe, and Mg) and organic matter to calculate a mean anthropogenic enrichment factor (EF) (Boës et al., 2011; Shotyk et al., 1996; Weiss et al., 1999). Recently Pb began to increase at McCargoe Cove and Chickenbone Lake ~90 yr BP (1860 AD) corresponding with the initiation of copper smelting on the Keweenaw Peninsula (Lankton, 2010) and the formation of a small mining town in the catchment of McCargoe Cove from 1875 to 1885 AD. Lead EF's continued to increase and eventually peaked between 0 and -30 yr BP (1950 and 1980 AD)(Figure 2-13), likely as a result of the use of leaded gasoline and the global rise in Pb emissions (Pacyna and Pacyna, 2001). The removal of lead additives from gasoline and the closure of the mining and smelting industries in the late 20th century led to substantial declines in Pb concentrations in sediments dated to after ~1980 AD. The absence of mining pollution in centuries leading up to European arrival is consistent with tree-ring age estimates of the overburden piles (Hagar, 1865; Whittlesey, 1863), which suggest that they were deposited at least centuries prior to the middle 19th century.

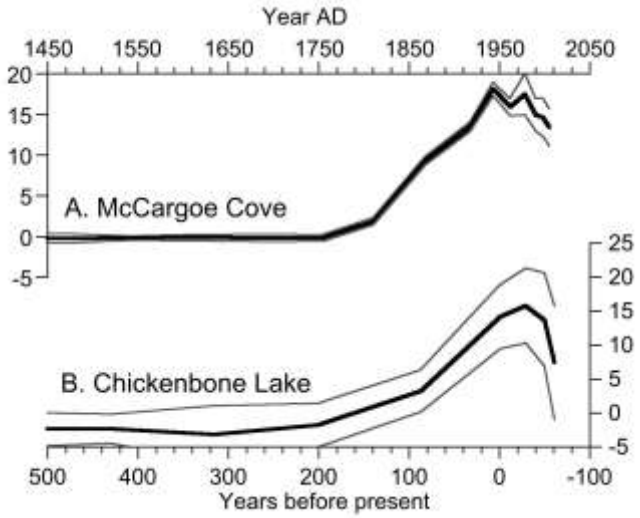


Figure 2-13 Recent lead enrichment factor record from (A) McCargoe Cove and (B) Chickenbone Lake.

Prior to recent increases starting around 90 yr BP (1860 AD), Pb remained at < 1 EF for the last ~5,400 years at McCargoe Cove and for the last ~8,000 years at Chickenbone Lake (Figure 2-14). Starting ~6500 yr BP, Pb EF values began to increase in McCargoe Cove sediments at an average rate of ~ 0.2 % yr^{-1} to a value of 11 by ~5400 yr BP. Prior to 6500 yr BP Pb EF values at McCargoe Cove were < 2 EF. This Pb EF increase does not appear to be recorded at Chickenbone Lake. At Chickenbone Lake higher Pb EF values (~5) occur prior to 8000 yr BP and are associated with elevated levels of Ti, Mg, and Fe suggesting that they are related to heightened inputs from weathering. In addition, the reference metals record highly disparate trends over this time, therefore the 95% confidence intervals for the mean EF value is wide and fall below 1 EF. The lack of a prehistoric Pb EF increase in Chickenbone Lake suggests that the Pb EF increases recorded at McCargoe Cove were local (Figure 2-14).

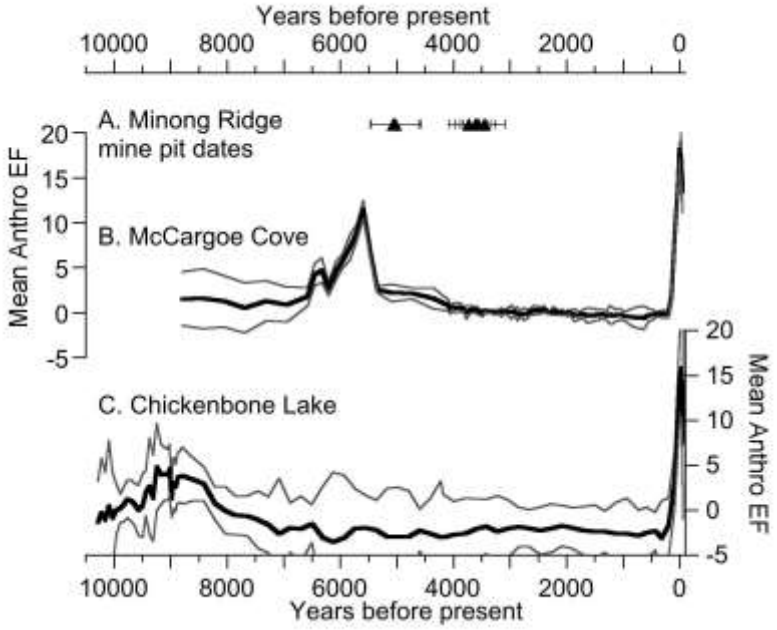


Figure 2-14 Minong Ridge mine pit radiocarbon ages (A). Prehistoric lead enrichment factor record from (B) McCargoe Cove and (C) Chickenbone Lake.

2.2.4.5 10% HNO_3 versus aqua regia analysis of sediments from 6500 to 5400 yr BP

Aqua regia extractions were conducted in order to measure metals that are strongly bound in the sediments. These were compared with metal concentration data from the 10% HNO_3 extractions (i.e., sorbed fraction) taken from the same homogenized sediments. Since the concentrations of metals derived from the aqua regia extraction are non-sequential they still contain the sorbed metal fraction. The sorbed fraction is subtracted out using the 10% HNO_3 metals concentration data derived from the same sample. This resulting value is referred to as the difference (Figure 2-15). Higher difference values are interpreted to be the result of a higher mineral component relative to the sorbed fraction of metals.

Several observations can be made from the comparison between the metals derived from the aqua regia versus the 10% HNO_3 extraction. All the samples contain higher concentrations of metals in the aqua regia extraction, except Cu. Copper concentrations are about equal in both extractions because the Cu is likely in the form of an oxide and/or associated with organic matter, therefore equally as soluble in both the 10% HNO_3 and aqua regia extraction (Figure 2-15). Titanium concentrations are much higher in the aqua regia extract versus the 10% HNO_3 extract but still decrease ~1000 μg g^{-1} from 6500 to 5400 yr BP indicating an overall decline in the delivery of Ti-related mineral matter during this time. Strongly bound concentrations of Pb, K, Mg, and Fe, all peak in concentrations ~5600 yr BP, indicating that greater fluxes of mineral-bound K, Mg, and Fe. However, the difference values in Pb do not increase, indicating that Pb strongly bound in sediment changed little over 6500 to 5400 yr BP (Figure 2-15). In addition, the peak in sorbed K concentrations ~5800 yr BP comes before the peak in strongly bound in K ~5600 yr BP. Together this suggests that peaks in sorbed Pb and K concentrations were not associated with changes in mineral matter.

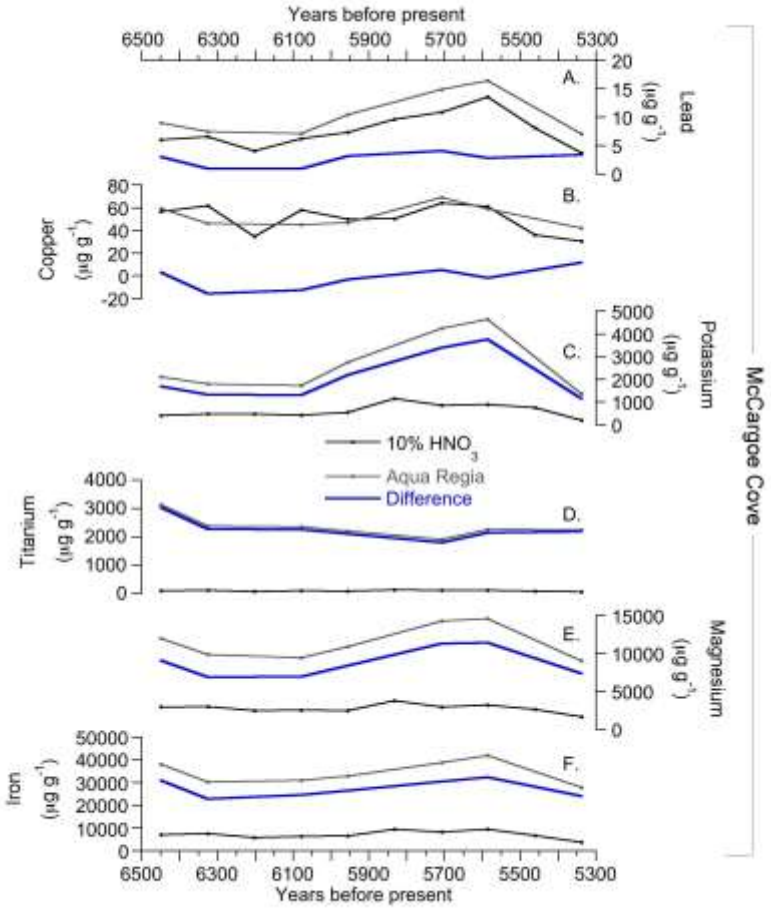


Figure 2-15 Concentrations of lead (A), copper (B), potassium (C), titanium (D), magnesium (E), and iron (F) in the Aqua Regia and 10% HNO_3 extraction from sediments deposited from ~6500 to 5400 yr BP in McCargoe Cove.

This analysis suggests that higher mineral-derived fluxes of metals were delivered to the sediment by 5600 yr BP, however the rise in sorbed Pb and K do not appear to be associated mineral matter. In the case of Pb, particulate size is inversely related to solubility in acids (Lindberg and Harriss, 1981), thus inputs of sorbed Pb probably included small (≤0.4 µm) particulates or other Pb compounds that are associated with mining and annealing. In addition, K sources derived from burning wood, such as KOH, dissolve in water forming ions that can

sorb to exchange sites in the sediments. Therefore the inputs of K derived from wood smoke and dissolved potash, would not necessarily influence the delivery of mineral bound K. In general, this analysis is consistent with input of copper mining and annealing derived Pb, Cu, and K compounds that are not associated with changes in mineral matter delivered to the lake.

2.2.4.6 Comparison with Minong Ridge mine pit dates

I compared Pb EF values at McCargoe Cove with published radiocarbon dates of charcoal recovered from pit mines on Minong Ridge (Table 2-8). Two radiocarbon dates obtained from charcoal preserved at the bottom of mine pits on Minong Ridge (Crane and Griffin, 1965) correspond to periods of Pb increases in the sediment of McCargoe Cove, however the other four reported dates appear to post-date the peak in Pb EF values. Therefore, I propose that these dates (Table 2-8), and potentially other radiocarbon dates from the mine pits and trenches (Crane and Griffin, 1965), mark the infill of the mine pits or possible contamination by more recent carbon (producing radiocarbon dates younger than the age of deposition), rather than being reflective of the active copper mining period.

Table 2-8 Radiocarbon dates from Minong Ridge

Sample*	Site	Material	^{14}C yr BP	Error
M-1384	Isle Royale, Minong Site	charcoal	4420	150
M-1390	Isle Royale, Minong Site	charcoal	4400	150
M-1387	Isle Royale, Minong Site	charcoal	3220	130
M-1388	Isle Royale, Minong Site	charcoal	3460	130
M-1389	Isle Royale, Minong Site	charcoal	3310	130
M-1385	Isle Royale, Minong Site	wood	3360	130

*All dates are from Crane and Griffin (1965)

2.2.5 Conclusions

Increasing metal pollution associated with copper mining near McCargoe Cove beginning ~6500 yr BP supports archaeological evidence for copper metalworking by at least the Early Archaic Period (Pleger and Stoltman, 2009). The rapid decrease in metal pollution inputs from 5500 to 5400 yr BP suggests an abrupt decline in mining/annealing activities at this location. The lack of any detectable increase in Pb, Cu, or K concentrations at Chickenbone Lake suggests that the metal emissions and mining activity were localized. In addition, multiple extractions conducted on sediments preserved from 6500 to 5400 yr BP, indicate that inputs of Pb and K, likely included particulates and soluble compound from burning wood, suggesting that the metals were delivered through some combination of dissolved forms delivered in groundwater and atmospheric deposition.

3.0 KEWEENAW PENINSULA RECONSTRUCTIONS

3.1 INTRODUCTION AND BACKGROUND

Surveys of the Keweenaw Peninsula during the middle and late 19th century identified thousands of mine pits with widespread evidence of prehistoric human activity in the form of hammerstones, copper artifacts, and overburden piles concentrated along the ~100 km copper-bearing ridge in the interior of the peninsula. Here, I use sediment cores from five lakes, known as Boston, Seneca, Copper Falls, Medora and Manganese (Figure 3-3-1), to demonstrate that on a local scale, measurable levels of atmospheric lead (Pb) pollution were generated at discrete time intervals by societies on the Keweenaw Peninsula starting as early as 9,500 years ago. I applied anthropogenic enrichment factor equations to metal records from the five lake sediment sequences to estimate past changes in human-related Pb inputs to the lakes.

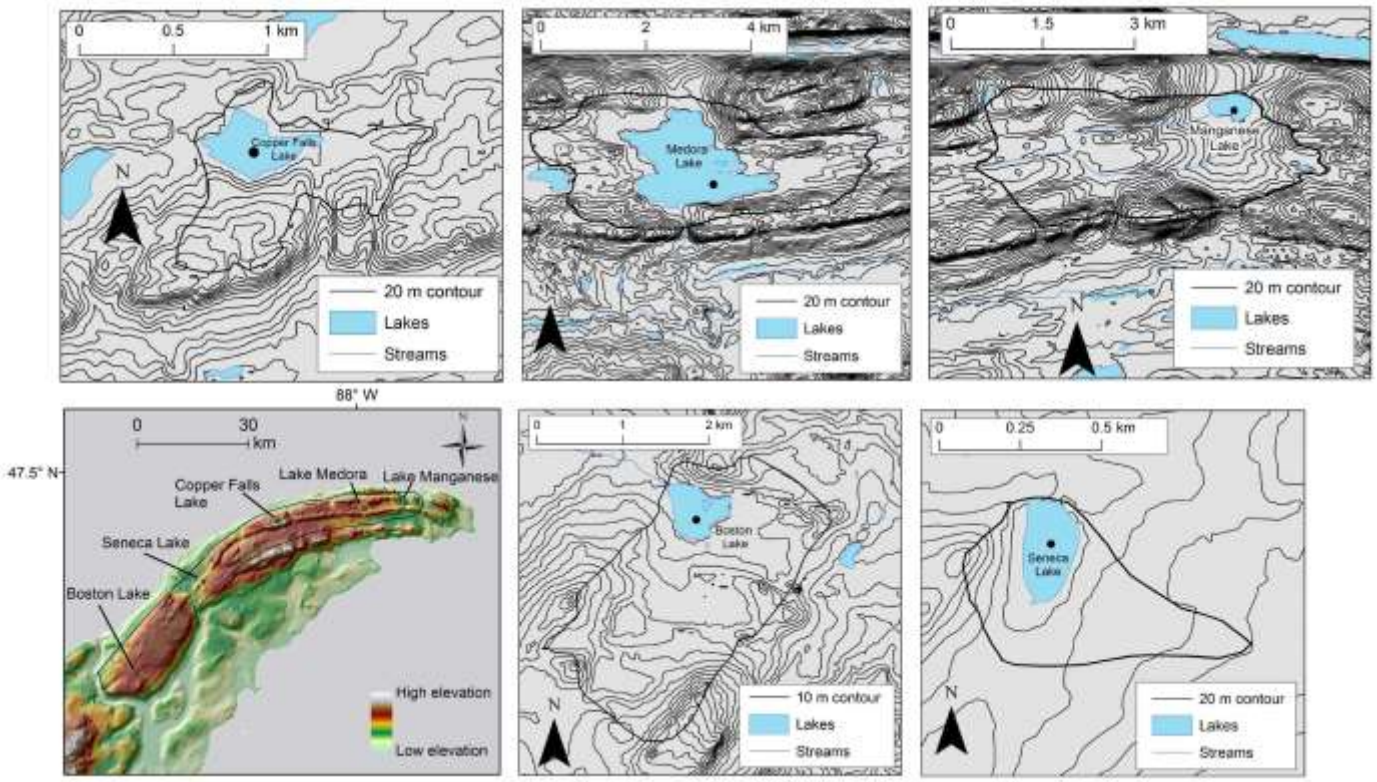


Figure 3-3-1 (Top left-right) Watershed maps from Copper Falls Lake, Lake Medora, and Lake Manganese. (Bottom left-right) Digital elevation map of the Keweenaw Peninsula with study lakes and watershed maps from Boston and Seneca Lake.

3.1.1 Overview of lead stable isotopes in lake sediments

The stable isotopes of lead were measured in the both weak and strong acid sediment extractions before, during, and after one prominent well-dated Pb spike occurring ~5900 yr BP at Copper Falls Lake, including one sample from the modern period. The stable isotope data were then compared with published Pb isotope values for mine ores and loess from North America to determine if source changes are detectable ~5900 yr BP. Naturally occurring lead has four stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) that can be used to track changing sources of Pb in the sediments because the relative abundance of the isotopes is specific to the source of the Pb.

Anthropogenically-derived Pb in lakes from smelting and fossil fuel combustion can have a different isotopic signature than natural Pb inputs from the lake's catchment bedrock. For example, stable isotopes of Pb have been shown to record sources changes in Pb to lakes in Quebec from smelting lead in the Upper Mississippi Valley (Gobeil et al., 2013). In Europe, stable isotopes of Pb in sediment have been used to track changing sources of Pb to Swedish lakes over the last 3000 years, including changing sources during Roman Times (Brännvall et al., 2001). Strong acid extraction can liberate metals bound in mineral lattices, which can have different isotopic compositions than sorbed metals which are sensitive to anthropogenic inputs (Graney et al., 1995). Therefore both a strong (6 N HCl) and weak (1 N HCl) acid extraction techniques were utilized and measured to determine the isotopic composition of both the strong and weak acid fraction of Pb in the sediment from Copper Fall Lake.

3.1.2 Study sites

The principle copper-bearing rock is the Middle Proterozoic Portage Lake Volcanic unit which is mainly composed of metamorphosed basalt flows (Rosemeyer, 2009). Historic mining on the Keweenaw Peninsula began in 1843 AD, expanded until 1920 AD, and declined until 1997 AD when mining ended (Lankton, 2010). Early mining of the Portage Lake Volcanics focused on the highly-pure native copper veins exposed by glacial erosion, with later mining efforts aimed at extracting copper found within vesicles in the bedrock (amygdaloidal) and copper sulfides (Cu_2S, CuS)(Lankton, 2010; Rosemeyer, 2009). The Charles Whittlesey "Outline Map Showing the Position of the Ancient Mine Pits" accurately portrayed location of

the ancient mines, but it does not note surficial deposits that could inhibit direct access to bedrock (Whittlesey, 1862). Therefore, I incorporated surficial geology maps to highlight regions where bedrock is exposed at the surface (2.1.3). A comparison of the Whittlesey map with recent geologic surveys confirms that most prehistoric mine pits were located on exposures of Portage Lake Volcanic bedrock (Figure 3-3-2).

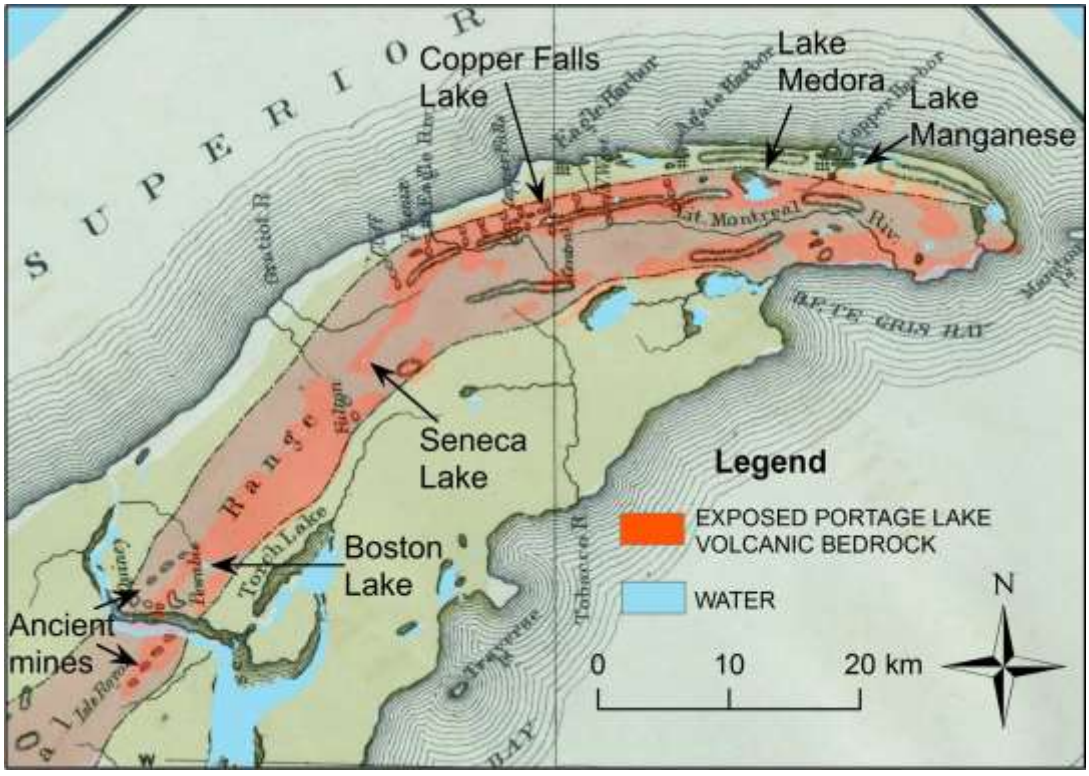


Figure 3-3-2 Georeferenced outline map of the prehistoric copper mines by Whittlesey (1862) in relation to exposed regions of Portage Lake Volcanic Bedrock with study sites noted.

Lake Manganese (47.454 °N, 87.883 °W, 0.5 km^2, 234 m asl), Copper Falls Lake (47.417° N, 88.192° W, 0.3 km^2, 392 m asl), Lake Medora (47.438° N, 87.976° W, 6.2 km^2, 307 m asl), Seneca Lake (47.316° N, 88.375° W, 0.2 km^2, 281 m asl), and Boston Lake (47.170° N, 88.528° W, 1.2 km^2, 324 m asl) are located along a ~60 km transect that follows the elevated Portage Lake Volcanic ridge within the interior of the Keweenaw Peninsula. Lake Manganese

(the northernmost lake) has a maximum depth of 7 m, receives inflow from two small streams that enter the lake from the south, and overflows through an outlet on the northern shore. Copper Falls Lake is topographically elevated, has a maximum depth of 3 m, and has no perennial inflow or outflow. Lake Medora is the largest of the three study lakes; it has a maximum depth of approximately 7 m, no surficial inflow, and one outflow that drains to the south. Lake Manganese and Copper Falls Lake are situated in isolated catchments that were logged multiple times over the last ~150 years. The catchment of Lake Medora is primarily forested, with the exception of an asphalt highway on the southern shoreline and several seasonal residences. The catchment of Seneca Lake is primarily forested and does not contain any seasonal residences. The lake is about 2.6 m deep, has one intermittent overflow to the north, and is adjacent to an asphalt and dirt service road. Boston Lake is the southernmost site and is the shallowest lake (1.7 m). The lake contains at least one input stream and an outlet that drains to the west. The northern shoreline of the lake was used to dump rock waste from modern copper mining in the area. Presently the catchment of Boston Lake contains several roads, residences, and is the most disturbed watershed (Figure 3-3-1).

3.2 METHODS

3.2.1 Fieldwork

We collected sediment cores from Copper Falls Lake, Lake Medora, and Lake Manganese in June 2010 and from Seneca Lake and Boston Lake in June 2012. Surface sediments were recovered using a piston corer fitted with a 6.6 cm diameter polycarbonate tube. Surface sediments were extruded in the field at 0.5-cm intervals to a depth of 50 cm. Overlapping 1-meter long cores spanning the remainder of the sediment sequence were obtained from each lake using a modified Livingston corer. All cores were collected near the depocenter of the lake basin. The Copper Falls record consists of four 1-m overlapping drives that extend 3.8-m below the sediment-water interface. The Lake Medora and Lake Manganese records consist of three 1-m drives that extend 3.1-m and 3.0-m below the sediment-water interface, respectively. Boston and Seneca Lake consists of six and eight 1-m drives that extend to 5.3- and 6.9-m below the sediment-water interface, respectively.

3.2.2 Loss-on-ignition

In the laboratory the sediment cores were split into halves and sub-sampled at 3- to 5-cm intervals using a 1-cm^3 piston-core sampler. The sediments sub-samples were then dried at 60°

C for 48 hours to remove water. Organic matter and calcium carbonate content as a weight percentage were then measured by loss-on-ignition (LOI) using a muffle furnace at 550 °C for 4 hours and 1,000 °C for 2 hours (Dean, 1974; Heiri et al., 2001). The 1,000 °C burn indicates that carbonate minerals are not found in the sediments.

3.2.3 Radiometric dating

^{210}Pb assays interpreted with the Constant Rate of Supply (CRS) method (Appleby and Oldfield, 1978; Binford, 1990) to date the upper 20 cm of sediment from all three surface cores. Radioisotope (^{210}Pb, ^{137}Cs and ^{214}Pb) activities were determined by direct gamma counting using a high-purity, broad-energy germanium detector (Canberra BE-3825) at the University of Pittsburgh. Terrestrial macrofossils for radiocarbon dating were isolated from the sediment, pretreated following standard acid-base-acid procedures (Abbott and Stafford, 1996), and measured at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California, Irvine. Three, three, twelve, five, and three radiocarbon dates were obtained from the Boston, Seneca, Copper Falls, Medora and Lake Manganese sediment cores, respectively. We generated spline age-depth models with 95% confidence intervals using CLAM for R (Blaauw, 2010).

3.2.4 Metal analyses

Sub-samples for metal analyses were collected at variable intervals from the homogenous organic-rich sediments positioned above the deglacial sediments. The uppermost 20 cm of each core was sub-sampled for metal analyses at 1- to 2-cm resolution. Over the remaining lower sections of each core, sub-samples were obtained at 3- to 4-cm resolution. After initial analyses, the sediment record was re-sampled continuously every 1-cm through prehistoric intervals of interest. Sub-samples were frozen, lyophilized and homogenized prior to extraction from ~0.2 g of sediment with 10% HNO_3 by constant agitation at room temperature for 24 hours in 15 ml polypropylene tubes (Abbott and Wolfe, 2003). Acidified sub-samples were centrifuged and the resulting supernatant was used for metal measurements. Metal concentrations in the Copper Falls Lake supernatant were measured using a Perkin-Elmer Sciex Elan 6000 inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Alberta. Detection limits are (in $\mu g\ g^{-1}$) 0.03 for Pb, 0.03 for Cu, 6 for K, 0.09 for Ti, 2.00 for Mg, and 3.70 for Fe. The Lake Medora, Lake Manganese, Seneca Lake, and Boston Lake records were measured using the Perkin/Elmer NEXION 300X ICP-MS at the University of Pittsburgh (detection limit is $< 1\ \mu g\ g^{-1}$ Pb, Cu, K, Ti, Mg, Fe). In addition, standards, blanks, duplicates and reruns were conducted during analyses to ensure reproducibility within acceptable limits. Lead concentrations were applied to anthropogenic enrichment factor equations using Ti, Mg, Fe, and organic matter to produce four indices of human-derived lead enrichment (Boës et al., 2011; Martinez-Cortizas et al., 2002; Weiss et al., 1999). All four indices were then averaged to produce a mean anthropogenic enrichment factor (with 95% confidence intervals), hereafter referred to as EF. Anthropogenic EF values ≤ 1 are generally considered background levels. To investigate spatial patterns, the mean anthropogenic enrichment factor record from each lake was interpolated to

100-year time intervals in Matlab. Every 100-year time step from each record was then input into ArcGIS with associated latitude and longitude coordinates and interpolated using an Inverse Distance Weighting function. The interpolated was then limited by a boundary shapefile that runs along elevated Portage Lake Volcanic ridge in the interior of the Keweenaw Peninsula.

3.2.5 Portage Lake Volcanic bedrock analysis

One small piece of the Portage Lake Volcanic bedrock located near the southern shoreline of Copper Falls Lake was measured to characterize the metal composition of the copper-bearing bedrock on the Keweenaw Peninsula. The sample was stored in labeled Whirlpaks® for transport. In the laboratory, the samples were washed with deionized water, dried and shipped to ALS Minerals for total metal analysis (procedure ME-MS41).

3.2.6 Lead stable isotope measurements

Four sediment sub-samples that were analyzed for lead stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb). A 6 N HCl and 1 N HCl overnight extract was used to liberate both sorbed and strongly bound Pb in the sample. The samples were then dried, and the residue was dissolved in dilute HNO_3. The resulting supernatant was extracted and measured on a multi-collector inductively coupled plasma-mass spectrometer (MC-ICP-MS) at The Department of Geology and Geophysics at Yale University.

3.3 RESULTS

3.3.1 Age models

A total of 26 radiocarbon and 69 CRS ^{210}Pb dates were used to calculate the age-depth models for Manganese, Medora, Copper Falls, Seneca, and Boston Lake (Table 3-1, Table 3-2, Table 3-3, Table 3-4, Table 3-5, Table 3-6, Table 3-7, **Table 3-8**, Table 3-9, Table 3-10). The ages were input into the CLAM package for R (Blaauw, 2010; Stuiver et al., 2010) to generate a tension spline age-model and determine 95% confidence intervals for the interpolated ages (Figure 3-3-3).

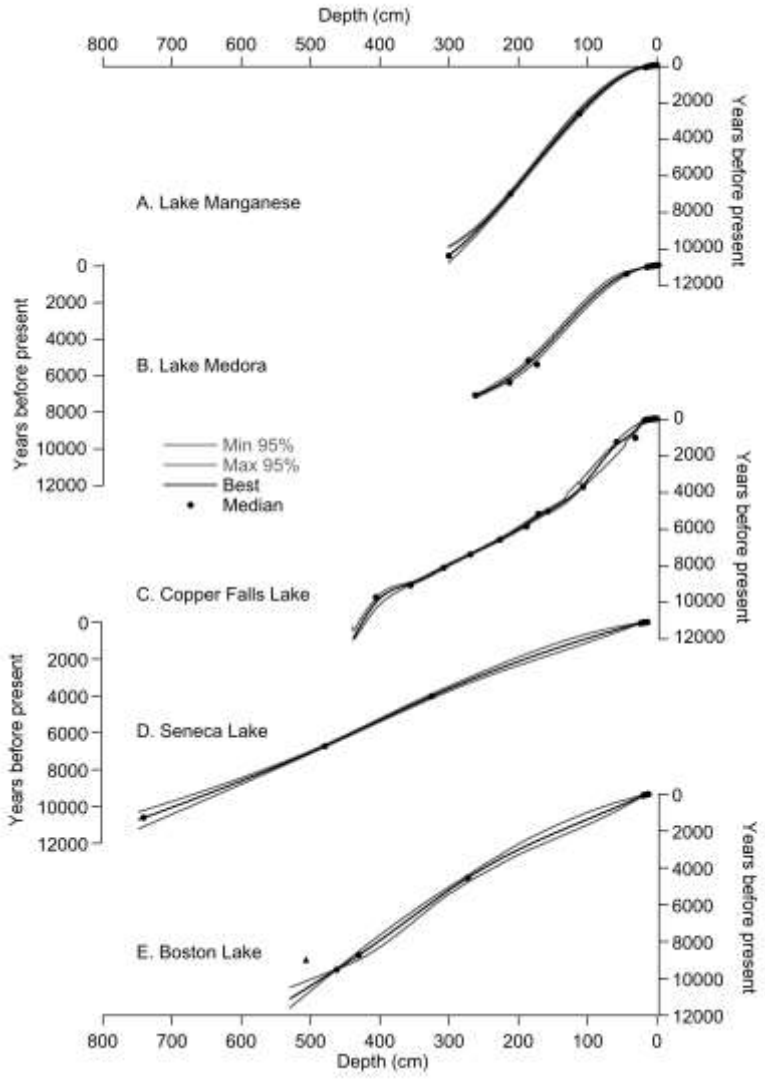


Figure 3-3-3 Age models for Lake Manganese (A), Lake Medora (B), Copper Falls Lake (C), Seneca Lake (D), and Boston Lake (E).

Table 3-1 Copper Falls Lake Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP[1])	Error (1 sig)
0.25	1.150	0.263	0.033	-59.0	1
0.75	1.070	0.202	0.044	-58.0	1
1.25	1.434	0.160	0.059	-57.0	1
1.75	1.550	0.195	0.076	-55.9	1
2.25	1.608	0.152	0.094	-54.5	1
2.75	1.620	0.187	0.109	-53.3	1
3.25	1.479	0.165	0.124	-52.3	1
3.75	1.530	0.198	0.139	-51.1	1
4.25	1.625	0.192	0.156	-49.6	1
4.75	1.610	0.195	0.190	-46.5	1
5.75	1.650	0.204	0.221	-43.2	1
6.75	1.500	0.147	0.258	-39.2	1
7.75	1.690	0.193	0.296	-34.0	1
8.75	1.169	0.120	0.333	-29.8	1
9.75	0.893	0.085	0.401	-22.9	2
11.25	0.964	0.132	0.436	-18.4	2
12.25	0.780	0.108	0.479	-13.2	2
13.25	0.926	0.110	0.527	-4.3	2
14.25	0.729	0.098	0.553	0.2	2
15.00	0.549	0.051	0.607	9.0	3
15.75	0.543	0.101	0.665	21.9	3
17.25	0.470	0.070	0.702	32.5	4
18.25	0.393	0.059	0.782	70.1	8

Table 3-2 Lake Medora Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP[1])	Error (1 sig)
0.75	1.428	0.151	0.077	-52.1	2
2.75	0.845	0.090	0.206	-41.7	2
4.75	0.462	0.056	0.382	-30.9	2
6.75	0.425	0.047	0.554	-16.5	3
8.75	0.277	0.035	0.702	-4.3	3
10.75	0.212	0.030	0.873	12.4	4
12.75	0.138	0.022	1.018	27.8	6
14.75	0.049	0.022	1.186	37.2	6
16.75	0.074	0.023	1.350	59.4	8

Table 3-3 Lake Manganese Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP^1)	Error (1 sig)
0.75	0.545	0.063	0.061	-58.5	1
2.75	0.554	0.061	0.251	-53.4	1
4.75	0.566	0.060	0.450	-46.8	2
6.75	0.415	0.045	0.682	-39.8	2
8.75	0.386	0.043	0.933	-30.9	2
10.75	0.354	0.040	1.200	-18.8	2
12.75	0.330	0.036	1.478	0.1	3
14.75	0.272	0.031	1.734	30.1	4
16.75	0.072	0.012	1.991	47.2	6

Table 3-4 Seneca Lake Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP^1)	Error (1 sig)
0.25	0.664	0.098	0.032	-61.1	1
2.25	0.900	0.104	0.088	-58.8	1
4.25	0.878	0.094	0.163	-55.6	1
6.25	0.954	0.099	0.256	-50.7	1
8.25	0.850	0.094	0.339	-46.2	1
10.25	0.943	0.101	0.412	-41.1	1
12.25	0.894	0.089	0.512	-33.0	2
14.25	0.882	0.105	0.603	-23.4	2
16.25	0.628	0.068	0.709	-12.4	2
18.25	0.566	0.072	0.826	4.3	3
20.25	0.327	0.042	0.948	21.4	3
22.25	0.096	0.019	1.074	29.1	4
24.25	0.116	0.022	1.199	41.6	5
26.25	0.147	0.036	1.304	64.1	6

Table 3-5 Boston Lake Pb-210

Depth (cm)	Unsupported Pb-210 (Bq/g)	Error (1 sig)	Cum. Wt. Flux (g/cm^2)	CRS Age (yr BP[1])	Error (1 sig)
0.25	0.868	0.111	0.035	-60.1	1
2.25	0.885	0.097	0.119	-55.1	1
4.25	0.658	0.072	0.229	-49.3	2
6.25	0.676	0.073	0.357	-40.6	2
8.25	0.691	0.074	0.483	-28.6	2
10.25	0.440	0.053	0.616	-16.9	2
12.25	0.346	0.042	0.754	-2.7	3
14.25	0.273	0.033	0.888	15.2	4
16.25	0.085	0.018	1.051	25.8	6
18.25	0.107	0.031	1.212	47.4	6
20.25	0.102	0.020	1.349	96.4	19

Table 3-6 Copper Falls Lake radiocarbon

UCIAMS #	Mean depth (cm)	^{14}C year BP	Error (σ)	Calendar year BP[1]	Error (95% upper)	Error (95% lower)
89125	31.25	1090	15	994	1052	958
84840	58.50	1260	20	1219	1267	1142
84841	106.50	3435	20	3685	3813	3639
84843	157.50	4435	20	5014	5253	4914
84842	171.50	4550	20	5156	5310	5074
101327	188.50	5110	70	5836	5994	5679
84844	226.50	5755	40	6555	6652	6453
84845	269.50	6455	20	7370	7424	7324
84846	308.00	7260	20	8091	8158	8015
84847	355.50	8125	20	9054	9120	9012
84848	405.50	8745	25	9716	9880	9597
84849	436.50	10255	25	12021	12103	11844

Table 3-7 Lake Manganese radiocarbon

UCIAMS #	Mean depth (cm)	^{14}C year BP	Error (σ)	Calendar year BP[1]	Error (95% upper)	Error (95% lower)
109371	112.00	2500	40	2582	157	216
109372	212.00	6110	20	6979	174	78
109373	301.00	9170	150	10365	387	463

Table 3-8 Lake Medora radiocarbon

UCIAMS #	Mean depth (cm)	^{14}C year BP	Error (σ)	Calendar year BP[1]	Error (95% upper)	Error (95% lower)
101328	46.25	365	35	423	79	107
109367	175.75	4670	110	5392*	214	351
109368	187.75	4560	50	5186	260	142
107556	214.75	5580	60	6367	116	83
101329	264.75	6155	30	7068	93	103

Table 3-9 Seneca Lake radiocarbon

UCIAMS #	Mean depth (cm)	^{14}C year BP	Error (σ)	Calendar year BP[1]	Error (95% upper)	Error (95% lower)
116875	327.5	3695	40	4035	4149	3914
122324	481.5	5905	25	6720	6783	6668
116876	743.5	9370	150	10614	11091	10244

Table 3-10 Boston Lake radiocarbon

UCIAMS #	Mean depth (cm)	^{14}C year BP	Error (σ)	Calendar year BP[1]	Error (95% upper)	Error (95% lower)
116873	273.5	4065	20	4546	4783	4444
131497	430.5	7890	70	8730	8983	8560
116874	462.5	8530	25	9522	9541	9489
122245	506.5	8055*	35	8988	9077	8776

3.3.2 Reference metals

Three elements (Ti, Mg, Fe) with varying geochemical properties and % organic matter were used to identify anthropogenic Pb variability relative to basin-specific background Pb delivery. Site-specific background values were calculated using the average of the entire record or in the case of the anthropogenic proxies the average value was taken from 5000 to 150 yr BP (when human influences appear to be minimal). Metals (e.g. Ti) and organic matter do not necessarily covary within and among the lake sites. This lack of covariance implies that inter- and intra-site disparity in the lake settings (e.g. differences in hydrology, productivity and bedrock composition) influence changes in background metals and organic matter concentrations on centennial timescales (Figure 3-4).

Despite the factors influencing inter-site disparities in reference metal concentrations, several broad patterns appear to be consistent between each lake, except Lake Medora which is limited to the ~6800 yr BP. Organic matter concentrations are low prior to 9000 yr BP, which is associated with higher concentrations of Cu, Ti, Mg, and Fe (Figure 3-4). This is in contrast to Pb and K concentrations, which remain relatively stable over these changes, except K concentrations are higher at Seneca Lake and Boston Lake prior to 9000 yr BP. In addition, Pb

and K record short increases in concentrations from 9600 to 5000 yr BP, which sometimes happen at different times at each lake, and are not associated with corresponding increases in Cu, Ti, Mg, and Fe. After about 8000 yr BP Cu, Ti, Mg, and Fe decline to relatively lower concentrations and organic matter concentrations increase in the sediments of all the lakes until modern times (Figure 3-4).

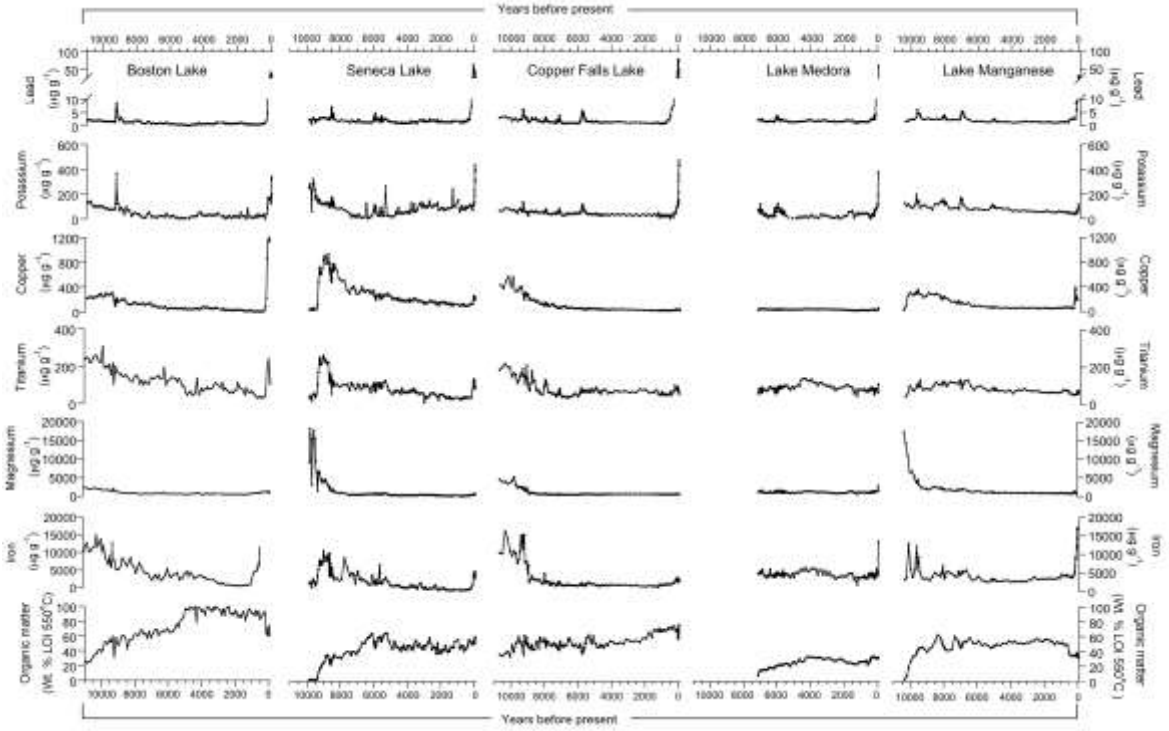


Figure 3-4 Sorbed metal concentrations and loss-on-ignition results from (left-right) Boston Lake, Seneca Lake, Copper Falls Lake, Lake Medora, and Lake Manganese.

3.3.3 Lead, Copper, and Potassium

Lead and K concentrations increase to values > 40 μg g^{-1} and > 300 μg g^{-1}, respectively, between 90 yr BP (1860 AD) to -55 yr BP (2005 AD), except for Lake Manganese which records a small increase in K concentrations in modern times. After ~6000 yr BP copper concentrations remain stable and below 200 μg g^{-1} at all study lakes. Only at Boston Lake and Lake Manganese are copper concentrations > 200 μg g^{-1} in modern sediments. Similarly, Pb and K remain at low and stable concentrations < 2 μg g^{-1} and < 200 μg g^{-1} for the previous 5,000 years. From about 9600 to 5000 yr BP, Pb and K record short century-scale increase to values >2 μg g^{-1} and > 200 μg g^{-1}, respectively. Some Pb and K increases between lake sites (Copper Falls Lake and Lake Manganese) appear coincident, while at other lake sites (e.g. Boston Lake) increases in Pb appear to happen once and do not appear to coincide with other lake Pb EF increases (Figure 3-4).

3.3.4 Stable isotopes of lead at Copper Falls Lake

The bottom three samples from both Copper Falls Lake dated to ~2300, 5700, 6800 yr BP contained Pb stable isotope ratios that are generally the same in both the strong and weak acid extraction (Figure 3-5, Table 3-11). The top sample from -20 yr BP (1970 AD) differs in that the ^{206}Pb /^{204}Pb, ^{207}Pb /^{204}Pb, ^{208}Pb /^{204}Pb ratios are significantly less (18.6, 15.6, ~38.5) than the respective average values of 19.4, 15.7, and 39.2 in the 1 N HCl extraction and 19.5,15.7 and 39.4 in the 6 N HCl.

Table 3-11 Stable isotopes of lead from Copper Falls Lake

Depth (cm)	Age (yr BP)	Extract	^{206}Pb /^{204}Pb	σ error	^{207}Pb /^{204}Pb	σ error	^{208}Pb /^{204}Pb	σ error
11.3	-20	1N HCl	18.60	0.001	15.61	0.001	38.84	0.004
79.5	2300	1N HCl	19.40	0.007	15.70	0.006	39.17	0.014
189.5	5700	1N HCl	19.45	0.002	15.71	0.002	39.18	0.005
239.5	6800	1N HCl	19.46	0.004	15.71	0.003	39.21	0.008
11.3	-20	6N HCl	18.65	0.002	15.62	0.001	38.33	0.004
79.5	2300	6N HCl	19.48	0.071	15.64	0.056	39.32	0.138
189.5	5700	6N HCl	19.60	0.007	15.72	0.006	39.47	0.014
239.5	6800	6N HCl	19.50	0.030	15.66	0.026	39.28	0.063

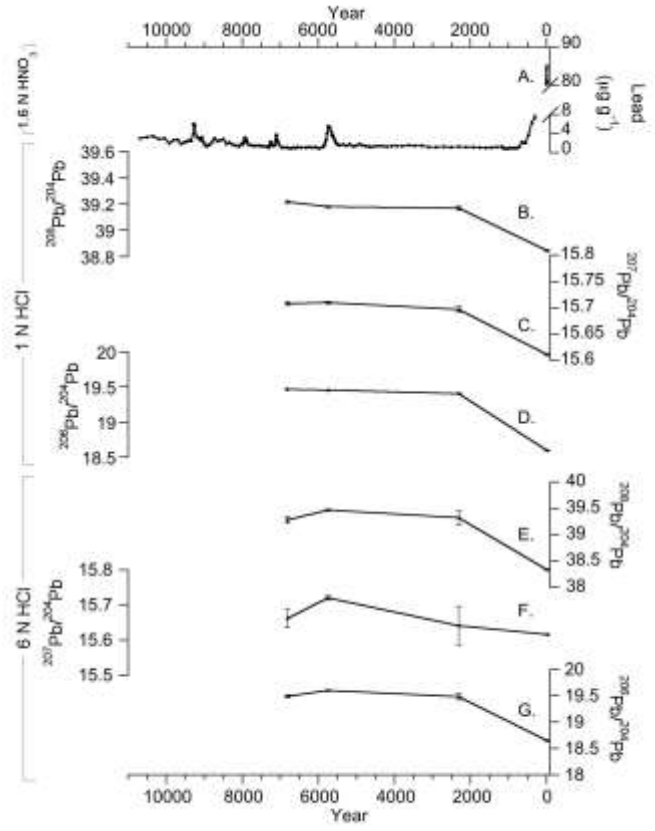


Figure 3-5 Lead concentrations (A) compared against the stable isotopes of lead in both sorbed (B-D) and strongly (E-G) bound the sediment of Copper Falls Lake.

3.3.5 Portage Lake Volcanic bedrock metal concentrations at Copper Falls Lake

Bedrock samples collected near the shoreline of Copper Fall Lake contained concentrations of Pb, Cu, and K around ~4, 93, and 400 μg g^{-1}, respectively. Titanium, Mg, and Fe concentrations were ~2,100, 11,500, and 45,400 μg g^{-1} (Table 3-12).

Table 3-12 Portage Lake Volcanic bedrock metal concentrations

Site #	Pb	Cu	K	Ti	Fe	Mg
7*	4	93	400	2110	45400	11500

*All measurements are in μg g^{-1}.

3.4 DISCUSSION

Several metals with different geochemical properties and organic matter were used as references for the processes influencing the delivery and preservation of metals in the sediments. In general, higher concentrations of K, Cu, Ti, Mg, Fe when organic matter concentrations low before 9000 yr BP likely reflects enhanced chemical weathering of the bedrock and till that was recently deglaciated ~12,000 yr BP, indicated by the oldest reliable radiocarbon age at the base of the Copper Falls Lake core. Low organic matter concentrations likely reflect lower productivity in the lakes during this time. The gradual increase in organic matter concentrations is tracked by the reduction of K, Cu, Ti, Mg, and Fe after ~8000 yr BP. This indicates that chemical weathering rates decreased and/or productivity in the lakes and their watersheds

increased. Overall, Pb concentration appears to be insensitive to changes in organic matter concentrations and reference metals. Short increases in Pb concentrations are associated with K, which are not recorded in the reference metals, and appear to occur at different times in the lakes prior to 5000 yr BP, suggesting that processes driving these changes occurred locally and preferentially released metals that are not found in high concentrations in the Portage Lake Volcanic bedrock. Considering the location of the lakes to known ancient copper mine, we interpret changes in Pb and K in the context of human activity.

3.4.1 Proxies of human activities

Lead concentrations increase in the sediments starting around 1750 AD. These increases coincide with the onset of a lead smelting in Missouri during French Colonial times. After 1860 AD the sediment record abrupt increases (Figure 3-6). This change coincides with the opening of the first smelter on the Keweenaw Peninsula (Lankton, 2010). Lead values continue to increase at each lake and peak between 1950 and 1970 AD, likely as a result of the growth of the smelting industry, leaded gasoline emissions (Kovarik, 2005), and the global rise in anthropogenic emissions (Pacyna and Pacyna, 2001). After 1980 AD, Pb concentrations decrease in the sediments at each lake except for Lake Medora (Figure 3-6). The high correspondence with the written record and the low, stable concentrations of Pb in natural sediments indicates that it is a reliable indicator of human activities (Table 3-13). Therefore Pb is used as the primary proxy for ancient copper working.

Copper concentrations only increase at Boston Lake and Seneca Lake in modern times. This is likely because Boston Lake and Lake Manganese contain large watershed with

substantial amounts of waste rock from copper mining deposited near the shoreline. Other sites with small watersheds, such as Copper Falls Lake, do not have waste rock piles or mines in them therefore do not record Cu concentration increases in modern sediments. This is similar to findings at McCargoe Cove and Chickenbone Lake (2.2.4) in which McCargoe Cove records Cu increases in modern sediments whereas Chickenbone does not because the Chickenbone's watershed did not contain a mine or waste rock piles (versus Minong Mine adjacent to McCargoe Cove). Therefore I interpret Cu as a proxy for the chemical weathering of rock associated with the copper ore.

Potassium is the only other element that consistently tracks the trends recorded in Pb concentrations. Copper is used as a proxy of chemical weathering of waste rock (2.2.4.3) and it is not associated with the discrete increases in Pb and K recorded multiple times at several lakes in prehistory. This suggests that the processes driving Pb and K are not simply a process of chemical weathering of copper-bearing bedrock and soils in the catchment. Therefore a plausible mechanism must be invoked to explain the preferential increases in Pb and K, in the absence of Cu and other reference elements found in high concentrations in the bedrock (Table 2-5, Table 3-12). Burning biomass preferentially releases K and was likely emitted along with Pb during mining, annealing, and processing of the copper ore. This is consistent with findings from Isle Royale, and suggests that emissions from ancient copper mining probably included emissions from burning wood (Calloway et al., 1989; Eichler et al., 2009; Larson and Koenig, 1994; Misra et al., 1993)(2.2.4).

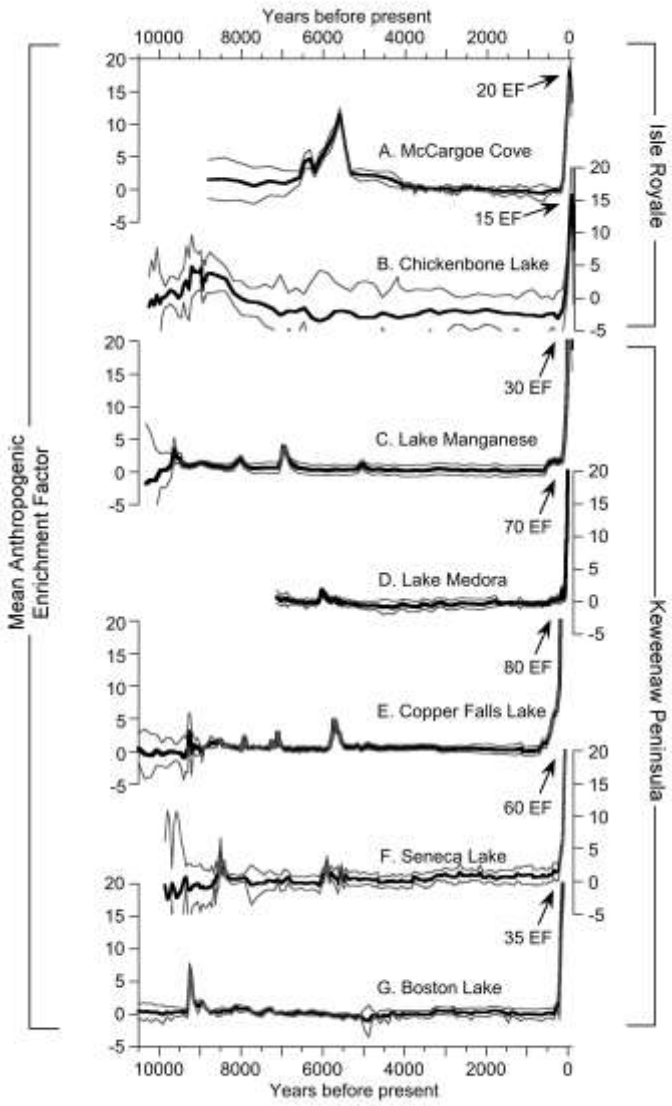


Figure 3-6 Prehistoric lead enrichment factors (EF) from (top-bottom) McCargoe Cove, Chickenbone Lake, Lake Magnanese, Lake Medora, Copper Falls Lake, Seneca Lake, and Boston Lake.

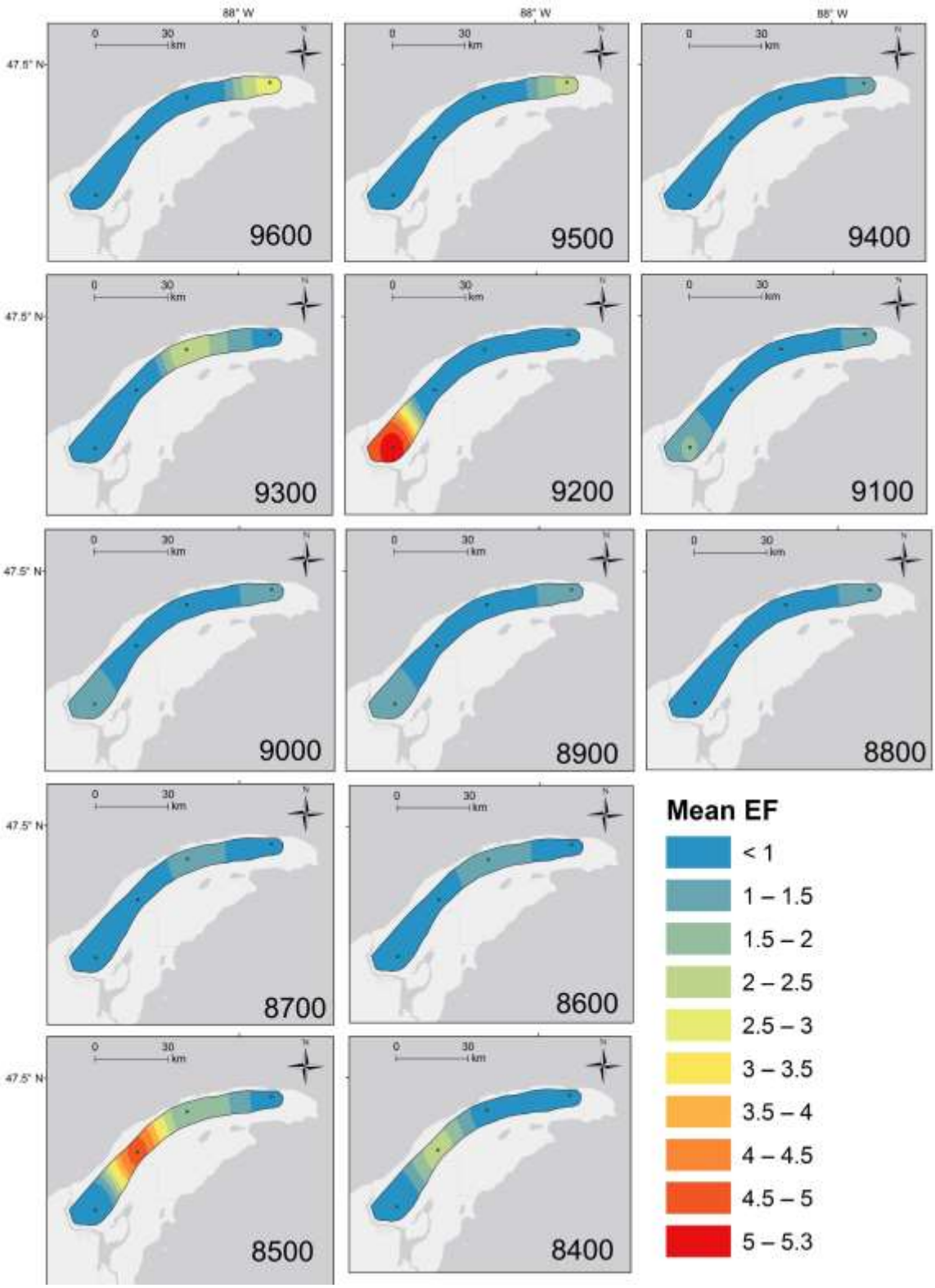


Figure 3-7 Phase 1 (9600 to 8400 yr BP) enrichment factor maps from the Keweenaw Peninsula.

3.4.2 Regional enrichment factor comparison

Lead was normalized to three reference metals (Ti, Fe, and Mg) and organic matter to calculate a mean anthropogenic enrichment factor (EF) to facilitate direct comparisons between records by accounting for average differences in metal concentrations between each lake (Table 3-13, Figure 3-6) (Boës et al., 2011; Shotyk et al., 1996). Lake sediment cores from the Keweenaw Peninsula (Lake Manganese, Lake Medora, Copper Falls Lake, Seneca Lake, Boston Lake) record increases after about ~100 yr BP, and subsequent declines after ~1980 AD, except Lake Medora, which records increases over the duration of the 20th century. Prior to this EF values remained stable over the last 5,000 years (Figure 3-6). Increases in Pb EF's are first recorded at Lake Manganese ~9600 yr BP, which shift to Copper Fall Lake by ~9300 yr BP (Figure 3-7). At ~9200 yr BP Pb EF emissions are detected at Boston Lake to south, during a time in which no other lakes record EF increases. From ~9100 to 8900 yr BP, EF increases are detected at both Boston Lake and Lake Manganese. From ~8700 to 8400 yr BP Pb emission appear to be concentrated at near Copper Falls and Seneca Lake. By ~8100 yr BP Pb EF activity shifts back to Lake Manganese and to Copper Falls area by ~7900 yr BP (Figure 3-8). After this time no detectable increases in Pb EF are found in the sediments until EF increases are detected again around 7100 yr BP at Copper Falls Lake and near Lake Manganese by 7000 yr BP (Figure 3-9). Around 6500 yr BP Pb EF's begin to rise in sediments at McCargoe Cove and peak around 5600 yr BP. Coincidentally at 5900 yr BP, Pb EF increases are again detected at Seneca Lake, which then shift to Copper Falls Lake by 5800 yr BP (Figure 3-10). Lead EF continues to be detected at Copper Falls Lake until about 5500 yr BP when it declines along with EF values from McCargoe Cove. Small increases are detected in Lake Manganese ~5000 yr BP, but after 5000 yr BP no detectable increase in Pb EF are detected at any site until ~200 yr BP (1750 AD).

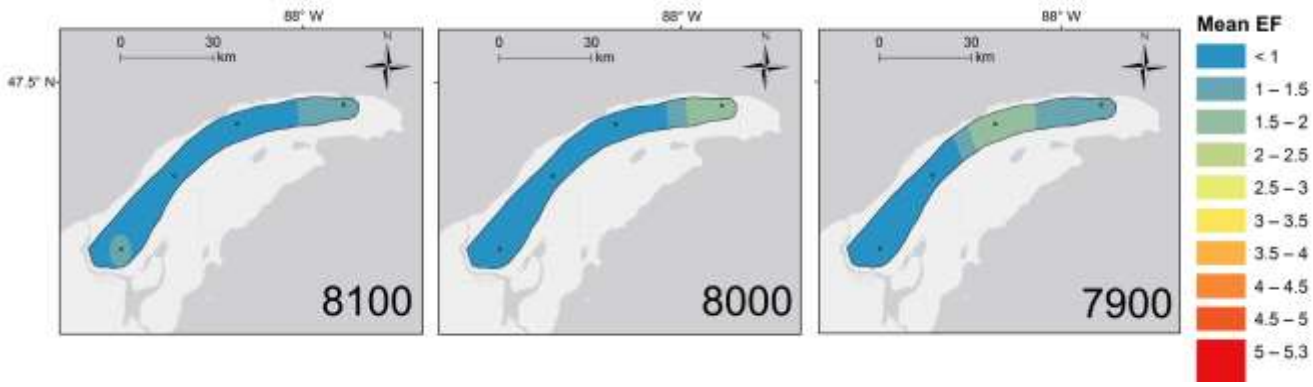


Figure 3-8 Phase 2 (8100 to 7900 yr BP) enrichment factor maps from the Keweenaw Peninsula.

Table 3-13 Background values

Lake	Pb (μg g^{-1})	Cu (μg g^{-1})	K (μg g^{-1})	Ti (μg g^{-1})	Mg (μg g^{-1})	Fe (μg g^{-1})	% Organic Matter
Lake Manganese	1.6	140	62	84	2285	5141	45
Lake Medora	2.1	37	28	85	1432	4596	25
Copper Falls Lake	1.2	108	32	71	613	2143	55
Seneca Lake	1.7	278	84	88	1745	2873	42
Boston Lake	0.9	99	23	123	1003	4896	71

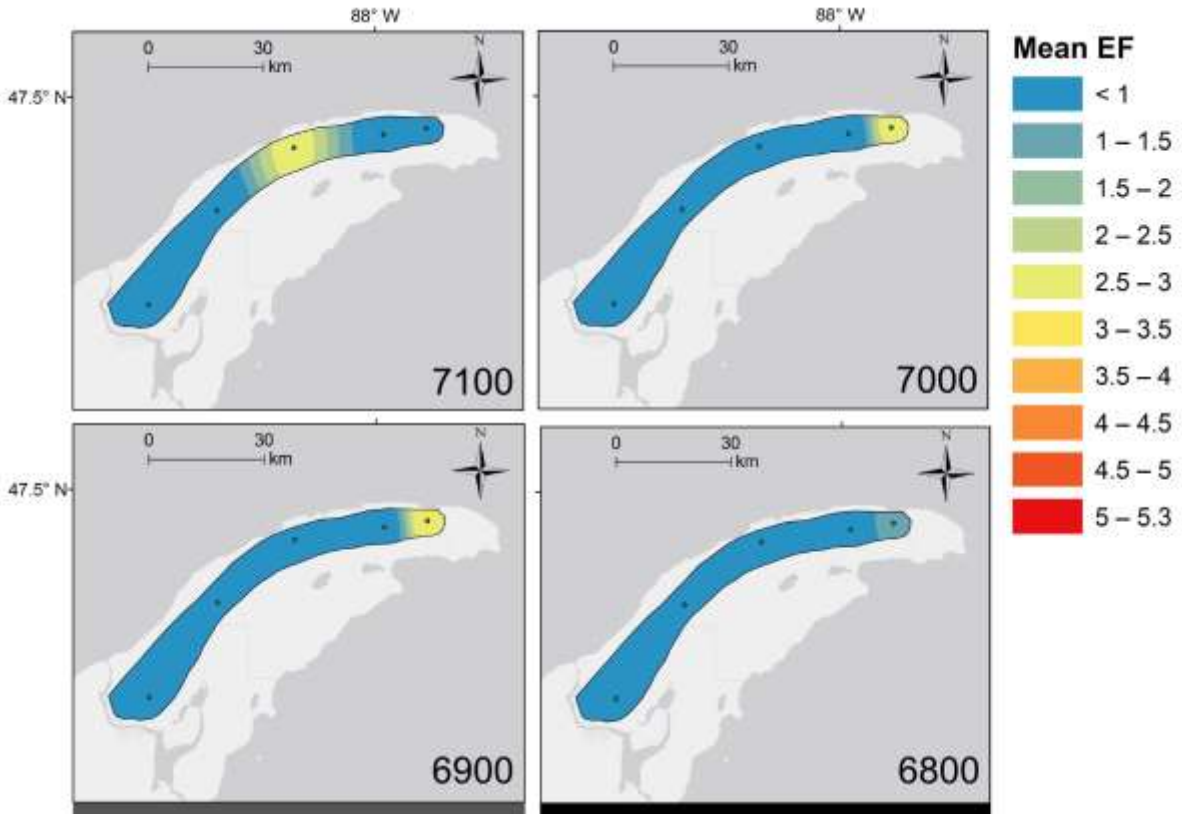


Figure 3-9 Phase 3 (7100 to 6800 yr BP) enrichment factor maps from the Keweenaw Peninsula.

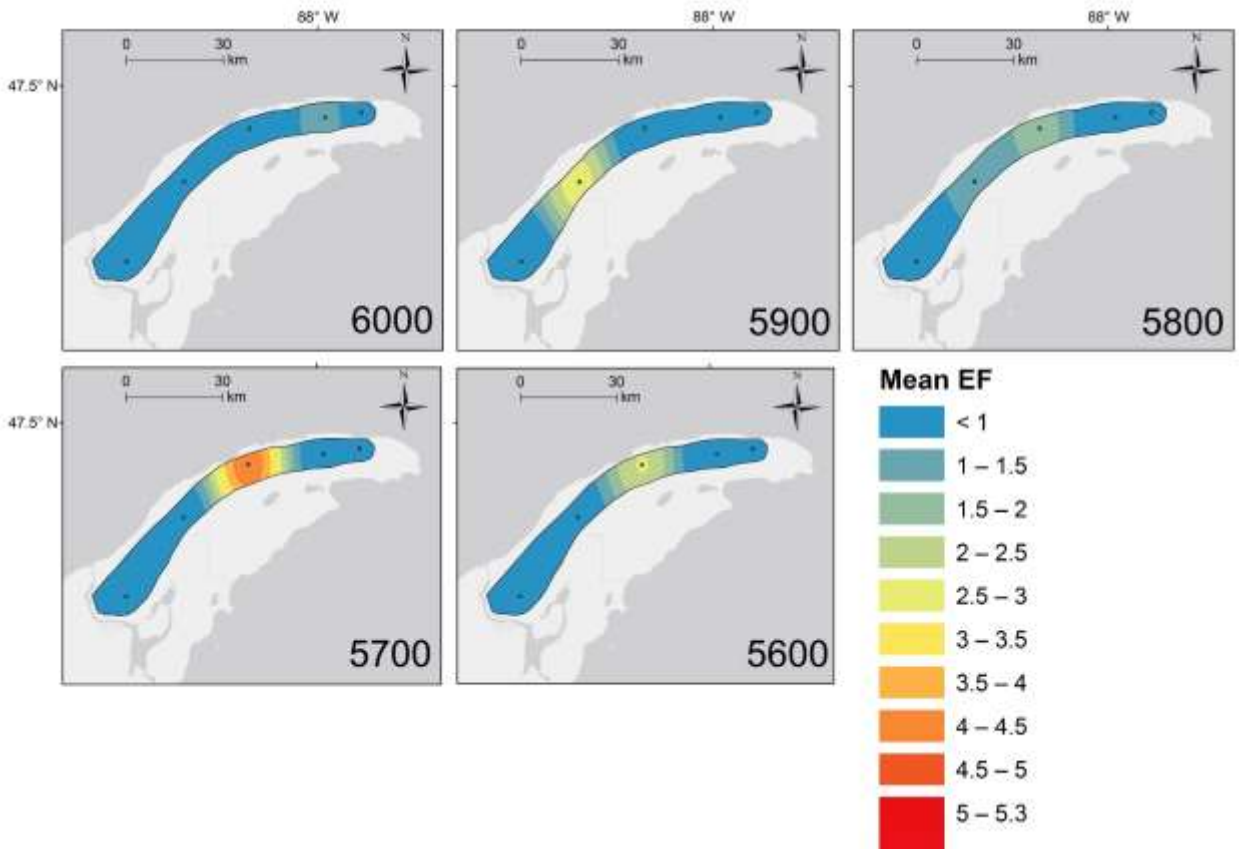


Figure 3-10 Phase 4 (6000 to 5600 yr BP) enrichment factor maps from the Keweenaw Peninsula.

3.4.3 Using stable isotopes of Pb to source pollution at Copper Falls Lake

The relative abundance of the stable isotopes of Pb is unique to geological source, therefore the stable isotopes of Pb can be used to track changing sources of Pb to lake sediments. The Pb isotopic composition of sediments is unique to the bedrock around small inland lakes, because the majority of natural Pb delivered to a lake is from the chemical weathering of soils and bedrock in the catchment (Renberg et al., 2002). Natural inputs of airborne Pb from outside the catchment are negligible and can be unstable (^{210}Pb) on long time scales, therefore the

concentration and isotopic composition of Pb remains relatively stable in the absence of external inputs from human activities.

At Copper Falls Lake, only the modern sample indicates a change in source, which is expected because it likely contains contamination with tetra-ethyl lead from burning gasoline, along with contributions from regional smelting metal ores both locally and regionally (Table 3-14). However, the bottom three samples do not show any significant variability, including the sample from 5600 yr BP, when Pb concentrations were five times greater than background values. This suggests that either the source of the Pb is the same as the bedrock or that the source of Pb came from the bedrock surrounding the lake. An external source of airborne Pb from an isotopically similar source is possible (Table 3-14), however the timing and length of the Pb concentration increases is different at each lake, suggesting that a large-scale dust event or perhaps volcanic or meteorite fallout is an unlikely source. The Pb was thus likely sourced from local bedrock, and was emitted along with K during mining and annealing activities. The emissions from copper mining appear to be local (2.2.4), which would explain the disparate timings of the Pb EF increases between sites, because mining likely shifted across the Keweenaw Peninsula through time.

Table 3-14 Regional lead stable isotope measurements

Sample	^{206}Pb /^{204}Pb	^{207}Pb /^{204}Pb	^{208}Pb /^{204}Pb	Source
Loess, Bluff 1 (B1)	19.45	15.75	39.81	Vermillion et al. (2005)
Loess, Bluff 2 (B2)	19.44	15.73	39.37	Vermillion et al. (2005)
Loess, Bluff 2 (B3)	19.28	15.63	39.58	Vermillion et al. (2005)
Missouri Leaded Gasoline	18.49	14.96	36.49	Rabinowitz and Wetherill (1972)
Ore, Balmat, New York	17.01	15.58	36.88	Brown (1962)
Ore, Ontario, Canada	13.35	14.57	33.27	Brown (1962)
Ore, Mine Lamotte (L1)	20.07	15.77	39.14	Goldhaber et al. (1995)
Ore, Mine Lamotte (L2)	20.70	15.85	39.79	Goldhaber et al. (1995)
Ore, Mine Lamotte (L3)	21.15	15.85	39.77	Goldhaber et al. (1995)

3.4.4 Implications of the Keweenaw Peninsula lake sediment records

Annealing activities associated with copper mining and processing on the Keweenaw Peninsula likely produced lower emissions than did the smelting practices in South America (Abbott and Wolfe, 2003), Europe (Renberg et al., 2002), and Asia (Lee et al., 2008). Despite lower emissions, discrete increases in Pb are recorded in lakes near mine pits during several periods from ~9600 to 5000 yr BP. In some cases, lead enrichments in sediments from nearby watersheds are offset by several hundred years. For instance, a prominent Pb enrichment found in the sediments of Copper Falls Lake (e.g. ~5700 yr BP) is absent at Lake Manganese and occurs at a significantly different time period (at 95% confidence) than the Lake Medora enrichment ~6300 yr BP. In sediment from ~8000 and ~7000 yr BP nearly simultaneous anthropogenic lead enrichments are recorded at Lake Manganese and Copper Falls Lake. These

reconstructions demonstrate that on a local scale, prehistoric Pb emissions grew and diminished multiple times over the course of decades to centuries. Developing additional lake records of Pb pollution will help to elucidate what is an apparently complex temporal and spatial pattern of human metalworking pollution

If prehistoric metalworking activity is proportional to pollution emissions then discrete increases in Pb between 9600 and 5000 yr BP (Figure 3-6) imply that human societies associated with the Old Copper Complex maintained the most intensive copper industry known in the prehistory of the Keweenaw Peninsula. No measurable increases in Pb concentrations occurred at any of the three lakes from ~5000 yr BP until the historic period, even though copper-using traditions (e.g. Hopewell; ~2100 to 1500 yr BP) existed at later periods in North America (Ehrhardt, 2009). During times in which anthropogenic Pb is absent in the lake sediments, people might well have still annealed or mined copper, although at a lower intensity that produced negligible emissions relative to background levels. For example, copper artifacts dated to the Woodland (e.g. ~1470 yr BP (Martin, 1993)) have been recovered on the Keweenaw Peninsula (Martin, 1993), but the sediment records suggest that the copper resources along the peninsula were not intensively mined or processed during this period. Given that Pb emissions appear to have been localized, it is possible that the mine pits that produced this copper have yet to be identified. Regardless, the existence of Pb pollution in the Archaic (~8000 to 5000 yr BP) on the northern Keweenaw Peninsula is noteworthy, because it predates all known anthropogenic lead emissions in the world (Cooke et al., 2008; Martinez-Cortizas et al., 2002; Renberg et al., 2002). Furthermore, the timing of the oldest anthropogenic Pb enrichments (~8000 yr BP in the Copper Falls Lake and Lake Manganese records) predate the oldest known evidence for copper

smelting in Eurasia (i.e. in Serbia, ~7000 yr BP (Radivojević et al., 2010)), indicating that early copper working techniques probably emerged at similar times at multiple locations.

Geochemical and artifactual records from Europe, South America, and Asia provide insight into the occurrence of metal-use and associated pollution. These studies have demonstrated that atmospheric Pb pollution occurred over the last 3000 years. The Keweenaw Peninsula lake records presented here provide evidence that prehistoric Pb pollution is detectable in North America and occurred over a period of about 3000 years starting by at least ~8000 yr BP. This predates archaeological evidence for agriculture in this region (Martin, 1999; Pleger and Stoltman, 2009), suggesting that early metal specialization and related metalworking pollution in prehistoric North America was not associated with or dependent upon agriculture.

3.4.5 Diminishing returns from copper mining?

The disparate timing of Pb EF increases at the four reconstruction sites (Figure 3-6) could be related to inherent uncertainties in the sediment age-models (Figure 3-3-3). Alternatively, the spatial and temporal pattern may be explained by how humans decide to look for and exploit resources. Specifically, as mining activity grew near lakes such as Boston and Copper Falls, and other localities around Lake Superior, we hypothesize that the most accessible (e.g. location, purity, workability) copper was targeted first, followed by other comparable areas. For example, our field observations on Minong Ridge and other written accounts noted that the Old Copper miners used the strike of the copper veins to predict the location of additional copper loads covered by shallow surficial deposits (Gillman, 1873; Whittlesey, 1863). As mining activity grew and the copper deposits were depleted and/or became more difficult to exploit, producing

decreasing returns (Tainter et al., 2006), the mine site would eventually be abandoned in favor of more accessible deposits. Thus, as the miners discovered and exploited new deposits in different locations, pollution loadings to the lake would shift through time and may not be detectable at distal sites. In some cases, multiple periods of Pb EF increases indicate that some localities (Copper Falls Lake, Lake Manganese) were worked over several temporally distinct periods. After mining was abandoned, pollution levels would decrease, consistent with geochemical evidence found in sediment cores from multiple mining locations. Despite thousands of years of mining, copper is still found in the region. Therefore, diminishing return rates from mining only partially explain the permanent reduction of mining pollution after 5000 yr BP.

3.4.6 Climate change and the end of copper mining?

Another line of evidence that could explain the rapid decline of mining pollution can be found in regional paleoclimate records from Elk Lake (45.890° N, 95.832° W) in western Minnesota (Smith et al., 1997; Smith et al., 2002), Crawford Lake (43.468° N, 79.949° W) in southern Ontario (Yu et al., 1997), and Fayetteville Green Lake (43.033° N, 75.967° W) in New York (Kirby et al., 2002). At Elk Lake the presence of shallow water ostracods (i.e. *Limnocythere staplini*) and higher carbonate $\delta^{18}O$ indicate the onset of dry conditions starting around 5400 yr BP. After ~5400 yr BP, low lake-levels and more saline water prevailed for about two centuries (Smith et al., 2002). In addition, low lake-levels and sediment carbonate $\delta^{18}O$ at Crawford Lake suggest a period of dry conditions and low lake levels beginning at ~5500 yr BP (~4800 ^{14}C yr BP) (Yu et al., 1997). Dry conditions at Crawford Lake persisted for ~3000 years, as evinced from a hiatus in sediment deposition from shallow water cores. At Fayetteville Green Lake, a reduction in the delivery of moist Gulf air masses and an increase in the frequency

of cross-continental, moisture-poor, low-$\delta^{18}O$ precipitation occurs after ~5200 yr BP indicated by a shift to more negative sediment $\delta^{18}O$ (Kirby et al., 2002). Interestingly, the onset of drier conditions at Elk Lake, Crawford Lake, and Fayetteville Green Lake coincide or follow the decline in Pb emissions at Seneca Lake, Lake Medora, Copper Falls Lake, and McCargoe Cove. When interpreted in combination, the sediment Pb reconstruction records from Isle Royale, the Keweenaw Peninsula, and paleoclimate proxies from around the Great Lakes provide tentative evidence that the regional cessation of more than 4000 years of mining pollution around Lake Superior coincided with the onset of sustained dry conditions in the Midwest (Figure 3-4).

3.5 CONCLUSIONS

Geochemical and artifactual records from Europe, South America, and Asia provide insight into the occurrence of metal use and associated pollution. These studies have demonstrated that atmospheric Pb pollution occurred over the last 3000 years. The Keweenaw Peninsula lake records presented here provide evidence that prehistoric Pb pollution is detectable in North America and occurred over a period of about 4000 years starting by at least ~9600 yr BP. This predates archeological evidence for agriculture in this region, suggesting that early metal specialization and related metalworking pollution in prehistoric North America was not associated with or dependent upon agriculture.

Metal pollution detected at locations on both Isle Royale and the Keweenaw Peninsula demonstrates mining activity occurred across the greater Lake Superior region from 6500 to

5400 yr BP. After 5000 yr BP, lake sediment records from McCargoe Cove on Isle Royale and the Keweenaw Peninsula do not contain any significant Pb increases until European settlement. Changing spatial and temporal patterns of pollution could be related to shifts in the location of copper mining activity during the Old Copper mining period. Therefore identifying and separating human from natural changes will improve interpretations of lake sediment proxies from the region. Notably the final cessation of Pb emissions at multiple lakes coincide with the onset of sustained dry conditions detected at several sites around the Great Lakes (Kirby et al., 2002; Smith et al., 1997; Smith et al., 2002; Yu et al., 1997), raising the possibility that metalworking activity associated with hunter-gatherer economies in North America were susceptible to influences of climate change.

4.0 HOLOCENE $\Delta^{13}C$, $\Delta^{15}N$, C/N RECORDS OF BULK ORGANIC MATTER FROM COPPER FALLS LAKE AND BOSTON LAKE

4.1 INTRODUCTION AND BACKGROUND

The stable isotopes of nitrogen (N) and carbon (C) in organic matter sedimented in lakes have been used to reconstruct paleoenvironmental change because both the production and preservation of organic matter is connected to changing hydrologic and ecological factors, such as lake-level change, vegetation, and nutrient input (Brenner et al., 1999; Finney et al., 2012; Hu et al., 2001; Meyers, 1997). The primary sources of organic matter in lake sediments include detritus from phytoplankton and other organisms growing in the water column. In addition, terrestrial organic matter from plants and soils can be transported into a lake. The contribution of these two sources is strongly controlled by primary productivity in the water column, land-plant productivity, and transport process. The relative contribution of these sources can be inferred through time using C/N ratios because terrestrial organic matter sources contain a higher proportion of C relative to algal sources (Meyers, 1997). However, the C/N signal can be confounded by biological communities living in the lake, transport process, and post-depositional diagenesis, especially in lakes with an oxic hypolimnia (Galman et al., 2008; Hodell and Schelske, 1998).

The C and N isotopic composition of organic matter can be used to infer productivity change in the lake because phytoplankton discriminates against $^{13}CO_2$ and $^{15}NO_3$ during uptake. The resulting organic matter that is transported to the basin therefore preferentially removes ^{12}C and ^{14}N from the dissolved inorganic carbon and nitrogen pools in the photic zone. As the CO_2 or NO_3 become depleted and isotopically heavier in surface waters, phytoplankton discriminate less against ^{13}C and ^{15}N. For instance, in a closed system, no fractionation occurs under CO_2 or N-limiting conditions. Thus increased or decreased productivity in a lake therefore should be reflected by an increase or decrease in the $\delta^{13}C$ and $\delta^{15}N$ (Goericke et al., 1994; Hodell and Schelske, 1998).

Besides the availability of light, which is controlled primarily by the length of the ice-free season and the depth of the photic zone, nutrients and redox conditions can also affect the productivity, preservation, and the C and N isotopic composition of organic matter (Meyers, 1997). In addition, shifts in the species of phytoplankton or the growth of N-fixing cyanobacteria under N-limiting conditions could result in more negative isotopes, which can also affect the $\delta^{15}N$ of organic matter. Changes in trophic structure within the lake can also influence isotopic composition of N because $\delta^{15}N$ increases by 3 to 4 ‰ with each trophic transfer (Minigawa and Wada, 1984; Peterson and Fry, 1987). However, fractionation of C isotopes with trophic level change is significantly less than that observed for N isotopes (Wada et al., 1987). Diagenesis can also affect the isotopic composition of C and N in organic matter, but it appears to affect the C isotopic composition less than N (Altabet and Francois, 1994a, b; Galman et al., 2009; Hodell and Schelske, 1998).

Changes in lake level can influence other factors such as nutrient inputs, preservation of organic matter, sedimentation rates, and sediment focusing (Finney et al., 2012). Substantial

lake-levels changes can have a large effect on productivity, and can complicate interpretation of C and N isotopic records as function of climate alone. For example, when conditions are wet and lake-levels increase, transport of dissolved organic carbon $\delta^{13}C$ derived from soils of terrestrial C_3 plants in the catchment is enhanced. Carbon from these sources is depleted (~-27 ‰) relative to the atmospheric C (~-8 ‰), therefore greater inputs of dissolved C from watershed soils should generally result in organic matter with lower $\delta^{13}C$, when all other factors remained unchanged (Finney et al., 2012).

The C and N isotopic composition of organic matter in lakes can be used to infer changes in source and trophic status as a result of inputs of N and phosphorous from human disturbances to the lake watershed (Brenner et al., 1999; Hillman et al., 2014; Wolfe et al., 2013). For example, increases in $\delta^{15}N$ in sediments to lake and wetlands has been attributed to reactive N seepage from sewage in groundwater, which has relatively heavy $\delta^{15}N$ values relative to nitrogen from biological fixation and lightening (Brugam et al., 2003; Elliott and Brush, 2006). In addition, deforestation and the resulting increase in erosion and soil organic carbon delivery to lakes can lead to higher C/N values and depleted dissolved carbon reservoir to the photic zone (Kaushal and Binford, 1999; Meyers, 1997).

Here I use the relative concentration (i.e., C/N) and isotopic composition of C and N from Copper Falls Lake and Boston Lake to make paleoenvironmental inferences over the last 10,000 years. Primary productivity is strongly controlled by to growing season lengths and hydrologic balance in these lakes; therefore the $\delta^{13}C$ and C/N are used to make inferences about the climate change at Copper Falls Lake and Boston Lake. In addition, previous work at Copper Falls Lake and Boston Lake has shown that sorbed Pb and Cu concentrations can be used to indicate the presence of mining near the lake (2.2.4,3.4), therefore the C and N isotopic composition of

organic matter was used to investigate whether land-use disturbances, such as deforestation, can be detected during periods in which mining occurred. Additionally, the $\delta^{13}C$ and C/N are compared with a previously published palynological record from Mud Lake (Booth, 2002) from the Keweenaw Peninsula to investigate changes in vegetation during paleoenvironmental shifts record in the sediments of Copper Falls Lake and Boston Lake.

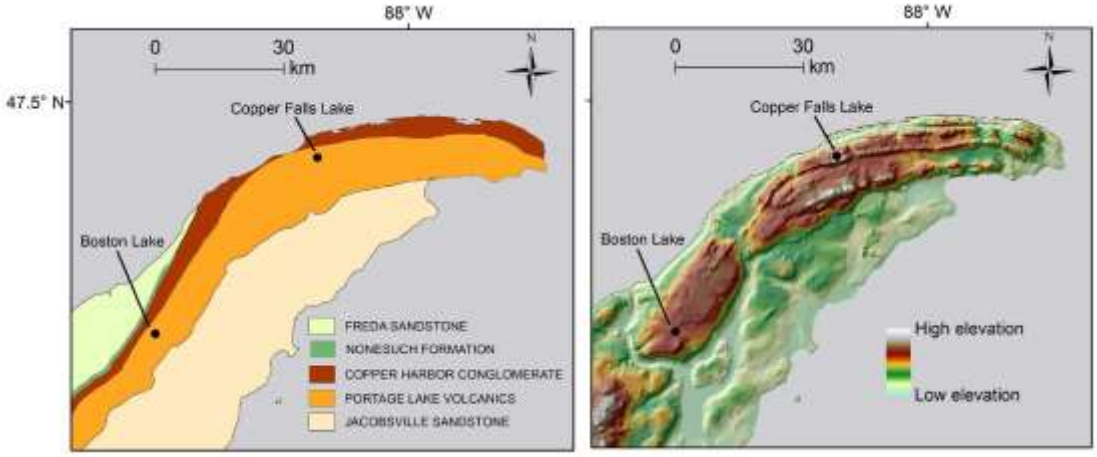


Figure 4-4-1 Bedrock (left) and digital elevation model (DEM) (right) map of the Keweenaw Peninsula with Boston Lake and Copper Falls Lake noted.

4.1.1 Study sites

Copper Falls Lake and Boston Lake were chosen for analysis because they are situated in isolated watersheds located near exposures of Portage Lake Volcanic bedrock that was mined in prehistoric times as indicated by Charles Whittlesey's map (2.1.3.3)(Whittlesey, 1862). Boston Lake contains a surficial inflow and overflow streams, whereas Copper Falls Lake presently contains no permanent surficial drainage. Both Copper Falls Lake and Boston Lake are shallow and contain watersheds (including surface area of the lake) with areas of 0.7 and 5.9 km^2, respectively, that are isolated from each other.

4.2 METHODS

4.2.1 Fieldwork

Sediment cores were obtained near the center of Copper Falls Lake and Boston Lake in June 2010 and June 2012, respectively. The water column in Copper Falls Lake was measured with a Hydrolab with sensors equipped for temperature, dissolved oxygen, pH, and conductivity. Sulfuric acid titrations were conducted on the surface waters of Copper Falls Lake to determine alkalinity. Hydrolab measurements and surface water titrations are not available from Boston Lake. In addition, surface soil and shoreline samples were recovered the watershed of Copper Falls Lake and at Minong Ridge on Isle Royale and stored in Whirlpaks during transport to the lab.

4.2.2 Radiometric dating

Sediment sub-samples from the extruded upper ~20 cm at each lake were frozen, lyophilized, and homogenized. The sediments were packed in petri dishes and sealed airtight. After a three-week equilibration period the sediments were counted on a gamma spectrometer at the University of Pittsburgh, Department of Geology and Planetary Science (see 3.3.1).

4.2.3 Loss-on-ignition

In the laboratory, 1 cm^3 sub-samples were taken at 1-cm intervals down core from Copper Falls Lake and at 5-cm resolution from Boston Lake and dried at 60° C for 48 hours. Loss-on-ignition (LOI) was measured by combusting the dried sediments at 550° C for four hours and 1000° C for two hours to determine weight percent organic matter and carbonate content (Dean, 1974; Heiri et al., 2001)(3.2.2).

4.2.4 Carbon and nitrogen analysis

Sub-samples for C and N isotope measurements were treated with 6 ml of 10% HCl overnight at room temperature to dissolve any carbonate minerals. The next day the sediments were centrifuged and resulting HCl supernatant was poured off. The sediment was then rinsed to neutrality, frozen, lyophilized, and homogenized prior to analysis.

Sub-samples from Copper Falls Lake (n=182) were analyzed using ECS 4010 (Elemental Combustion System 4010) interfaced to a Delta V advantage mass spectrometer through the ConFlo IV system at Idaho State University. The elemental analysis is done by an evolutionary "flash combustion/chromatographic separation techniques". The furnace temperature was kept at 1000°C, while the reduction oven was 650°C. The gases generated from the combustion of the samples are carried in a helium stream into a GC column held at 60°C. The gases then get separated before being diluted in the ConFlo IV and passed to the mass spectrometer for analysis. Isotope ratios of $\delta^{13}C$ from both Lakes are reported as ‰ values relative to the VPDB scale; whereas $\delta^{15}N$ values are reported as ‰ values relative to air-N_2. Three in-house standards (ISU Peptone, Costech Acetanilide and DORM-2) that are directly calibrated against

international standards (IAEA-N-1, IAEA-N-2, USGS-25, USGS-40, USGS-41, USGS-24, IAEA-600) were used to create a two-point calibration curve to correct the raw data. ISU Peptone and Costech Acetanilide are used to set up a two-point calibration line. A third standard (DORM-2) is used to monitor the accuracy of the data. The final data is corrected using a three-point calibration curve. Precision is <0.2‰ for $\delta^{13}C$ and <0.2‰ for $\delta^{15}N$.

Soils samples and sub-samples from the Boston Lake (n=84) core were analyzed using an IsoPrimeTM Continuous Flow Isotope Ratio Mass Spectrometer with universal triple collector. Peripherals include a Gilson GX271 autosampler and a Trace Gas system for cryogenic trapping of low concentration atmospheric gases, such as N_2O, CH_4, and CO_2. The analysis is done by an evolutionary "flash combustion/chromatographic separation techniques" using a EuroVector high temperature elemental analyzer. Isotope ratios of $\delta^{13}C$ from both Lakes are reported as ‰ values relative to the VPDB scale; whereas $\delta^{15}N$ values are reported as ‰ values relative to air-N_2. Two in-house standards (USGS-40, USGS-41) were used to calibrate the raw data. Precision is <0.3‰ for $\delta^{13}C$ <0.5‰ for $\delta^{15}N$.

4.2.5 Metal analyses

Sub-samples for metal analyses were taken at 2-cm intervals down the Copper Falls Lake core and at 5-cm intervals down the Boston Lake core. After preliminary analyses, intervals of interest were resampled continuously at 1-cm resolution (see 3.2.4). All the samples were frozen, lyophilized, and homogenized and ~0.1 g of dry sediment was used for geochemical analyses. The metals were extracted by mixing homogenized dry sediment with 10% sub-boil distilled trace metal grade HNO_3 in 15 ml polypropylene tubes and constantly agitated at room temperature for twelve hours. Metals extracted from sediments using dilute HNO_3 are sensitive

to inputs from human activities (Graney et al., 1995; Monna et al., 1999). Metal concentrations in the resulting supernatant were measured on an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at the University of Alberta and the Department of Geology and Planetary Science at the University of Pittsburgh (3.2.4).

4.3 RESULTS

4.3.1 Core descriptions and water column measurements

Coring resulted in the recovery of continuous sediment records that extend ~4.5 m and ~5.2 m below the sediment-water interface at Copper Falls Lake and Boston Lake respectively. The base of the cores consists of deglacial sediments that consist of minerogenic sediments rich in silt and sand that contain low concentrations of organic matter. Following the deglacial sequence, the sediments transition to organic-rich, brown, homogenous sediment that is preserved over the duration the record. Sample measurements presented in this study are from the homogenous organic-rich sediments positioned stratigraphically above the deglacial sediment sequence.

Hydrolab and sulfuric acid titration measurements of the Copper Falls Lake water column find a pH of 6 to 7, oxygenated hypolimnion, and an alkalinity of 8 mg l^{-1}. Modern water chemistry data from Boston Lake is not available (Figure 4-4-2).

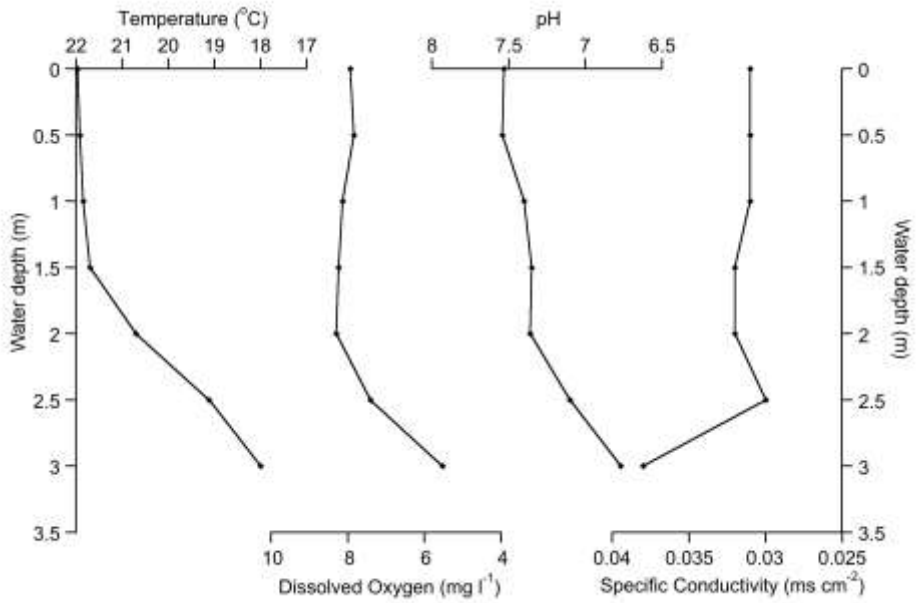


Figure 4-4-2 Hydrolab measurements of the water column at Copper Falls Lake Lake.

4.3.2 Carbon isotopes

Carbon isotope values are around -28‰ at Copper Falls Lake and Boston Lake ~10000 yr BP (Figure 4-4-3). Carbon isotope values increase and peak at values of -20‰ at ~7000 yr BP at Copper Falls Lake and at ~8000 yr BP at Boston Lake. After the peak, $\delta^{13}C$ values begin to decline. At Copper Falls Lake $\delta^{13}C$ abruptly dips to -27‰ for about 300 years after ~5500 yr BP, then rapidly increases to -25‰ ~4900 yr BP. At Boston Lake, this abrupt change in $\delta^{13}C$ is not recorded. Instead $\delta^{13}C$ values decrease to values of -27‰ by 6500 yr BP. At Boston Lake, $\delta^{13}C$ values remain stable around -27‰ until present, whereas at Copper Falls Lake values decline gradually since ~4900 yr BP. Around -70 to -60 yr BP (1880 to 1890 AD), $\delta^{13}C$ values decrease to -29 to -30‰ and remain at more negative values until 2012 AD.

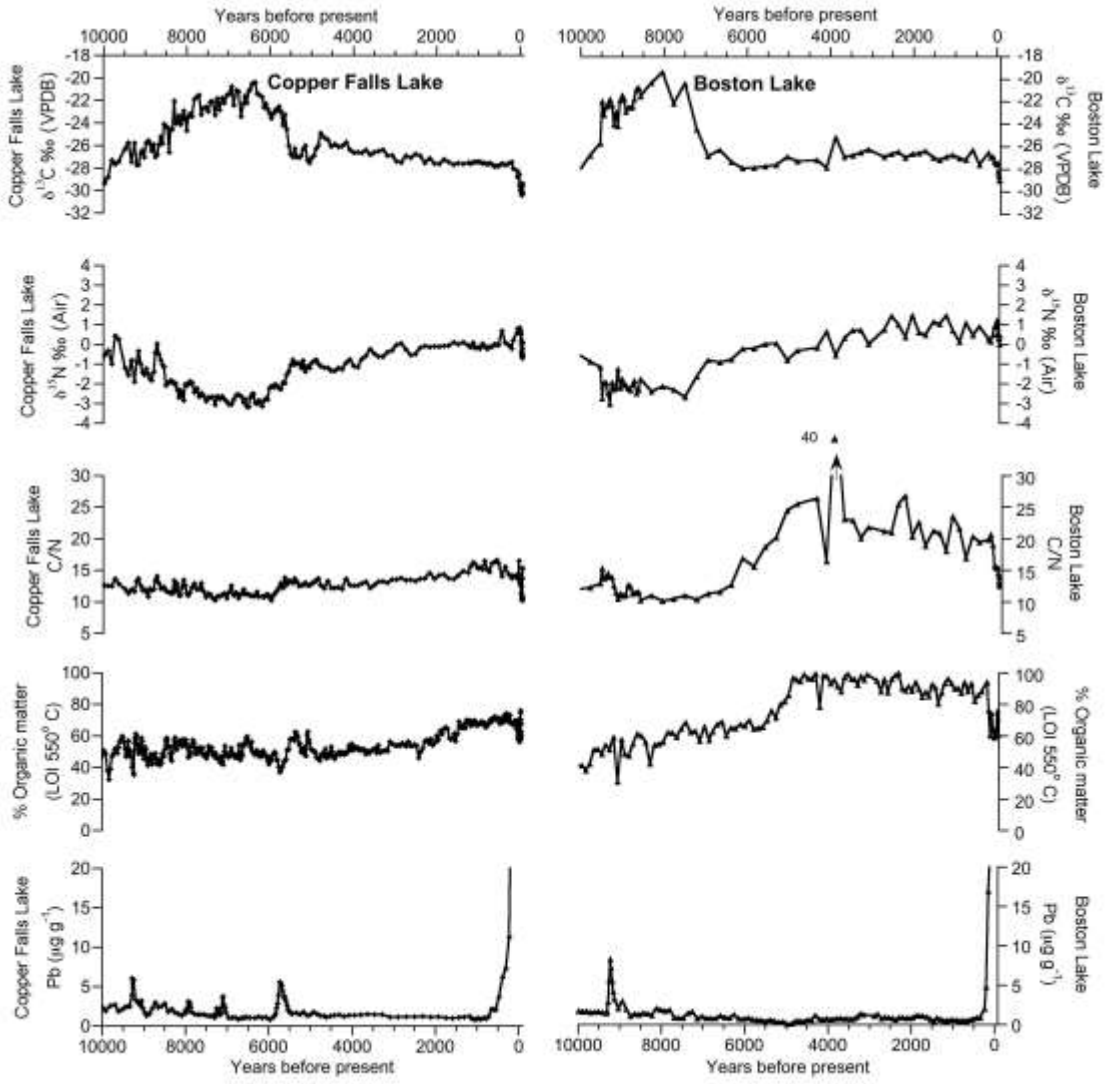


Figure 4-4-3 (Top-bottom) Holocene records of $\delta^{13}C$, $\delta^{15}N$, C/N, % organic matter, and sorbed Pb concentrations from (left-right) Copper Falls Lake and Boston Lake.

4.3.3 Nitrogen isotopes

Nitrogen isotope values were around -0.5‰ at Copper Falls Lake and Boston Lake by 10000 yr BP (Figure 4-4-3). After this time, $\delta^{15}N$ values began to decrease to low values of -3‰

at ~7500 yr BP at Boston Lake and ~6100 yr BP at Copper Falls Lake. Following this, $\delta^{15}N$ increase to 0 to 1‰ and remain stable over the duration of the Holocene.

4.3.4 Carbon/nitrogen ratios

Carbon/nitrogen ratios are between 10 and 15 at Copper Falls Lake and Boston Lake from ~10000 to 6000 yr BP. Around 6000 yr BP, C/N increase at both sites. Copper Falls Lake C/N remain elevated at concentrations of 15 to 16 for the duration of the Holocene, whereas Boston Lake C/N increase to values between 15 to 40, which gradually decrease after ~3900 yr BP (Figure 4-4-3).

4.3.5 Organic matter concentrations

Organic matter was around 40 to 60% at Copper Falls Lake and Boston Lake at the start of the record ~10000 yr BP (Figure 4-4-3). After this time % organic matter concentrations remain stable at Copper Falls Lake, then increase to 70% after ~5000 yr BP. At Boston Lake, organic matter concentrations increase gradually after 10000 yr BP. Then from ~5500 to 4900 yr BP, % organic matter abruptly increase to values. At Boston Lake, organic matter generally remain > 80 % after 4900 yr BP, but gradually decreases over the late Holocene.

4.3.6 Soil carbon and nitrogen analysis

A total of eleven soil and shorelines sediment samples, including three from the watershed of Copper Falls Lake were analyzed to characterize the isotopic composition of the soils. In general, the soil samples have average $\delta^{13}C$, $\delta^{15}N$ and C/N values of -26.77, 1.92, and 19.71, respectively (Table 4-1).

Table 4-1 Carbon, nitrogen isotope soil analysis

Sample	$\delta^{13}C$ (‰ VPDB)	$\delta^{15}N$ (‰ Air)	% C	% N	C/N
McCargoe Soil #1	-26.34	2.40	0.99	0.07	14.14
McCargoe Soil #2	-26.73	2.22	5.34	0.28	19.07
McCargoe Soil #3	-26.55	1.48	6.71	0.43	15.60
McCargoe Soil #4	-26.89	1.16	47.75	1.21	39.46
McCargoe Soil #5	-26.87	1.73	14.11	1.01	13.97
McCargoe Soil #6	-27.03	3.72	2.47	0.12	20.58
McCargoe Soil #7	-27.42	2.55	9.14	0.46	19.87
Copper Falls Soil #1	-26.62	3.04	5.30	0.36	14.72
Copper Falls Soil #2	-27.02	0.11	3.97	0.25	15.88
Copper Falls Shoreline #2	-26.57	0.33	6.65	0.37	17.97
Otter Lake Soil Sample	-26.45	2.33	39.79	1.56	25.51

4.4 DISCUSSIONS

4.4.1 Interpretive model

The concentration and isotopic composition of C in organic matter in sediment is of function productivity within lake, land-plant productivity, and transport processes (Meyers, 1997). At Copper Falls Lake and Boston Lake more negative $\delta^{13}C$ is associated with higher C/N

ratios. This is because the source of more negative $\delta^{13}C$ to the lakes comes from respirated carbon from the transport of soils in the watershed (Table 4-1), which contain higher concentrations of C relative to algal sources (Meyers, 1997). Conversely, when $\delta^{13}C$ values increase, C/N ratios decrease, indicating higher in-lake productivity and/or reduction of terrestrial C from soils in the catchment. The transport of soil carbon to the lake is presumed to be enhanced during higher precipitation; therefore we interpret lower $\delta^{13}C$ and higher C/N values as periods of relatively wet conditions, with dry conditions occurring during opposite conditions. Since $\delta^{15}N$ can be affected by diagenesis (Altabet and Francois, 1994a, b), changes in nitrogen-fixing land plants (Hu et al., 2001), soil type, and microbial communities (Evans, 2007), I interpret $\delta^{13}C$ and C/N as paleoenvironmental proxies that are sensitive to climate. In addition, these proxies are compared to sorbed Pb concentrations and a previously published pollen record (Booth, 2002) to determine the climate context of mining, and to investigate whether landscape disturbances can be detected from prehistoric copper mining landscape disturbances (Figure 4-4-4).

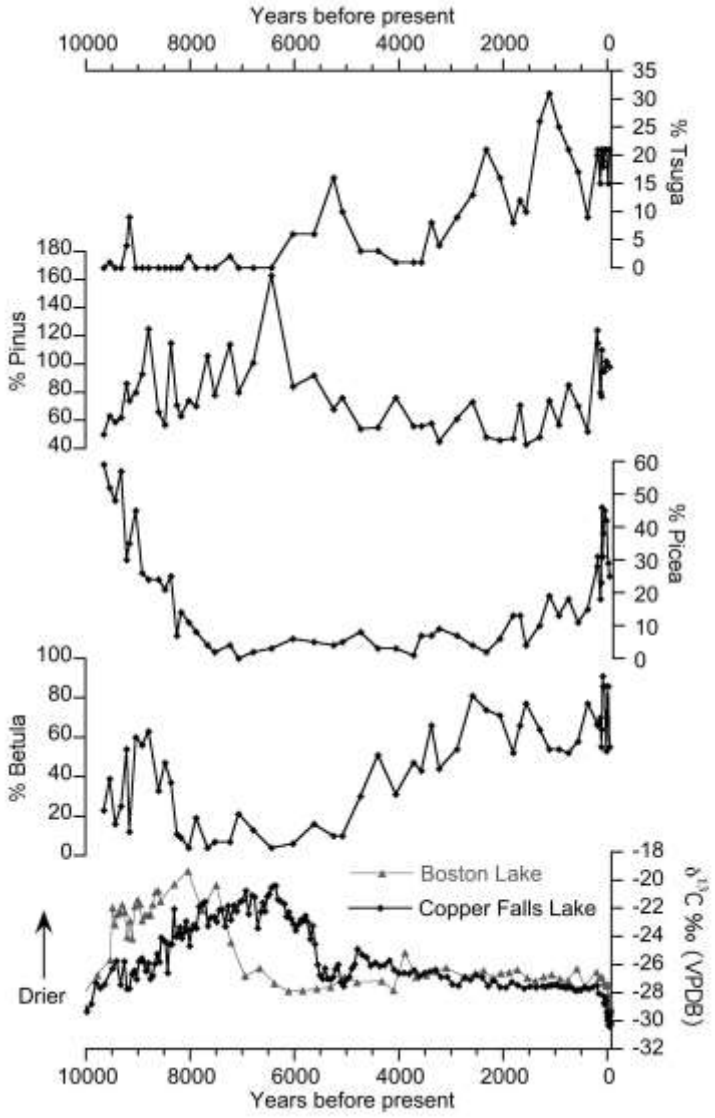


Figure 4-4-4 (Top-bottom) Palynological records, including *Tsuga*, *Pinus*, *Picea*, and *Betula*, from nearby Mud Lake (Booth, 2002) compared against the $\delta^{13}C$ records from Boston Lake and Copper Falls Lake.

4.4.2 Paleoenvironmental inferences from Copper Falls Lake and Boston Lake

The increase in $\delta^{13}C$ at Copper Falls Lake and Boston Lake from ~10000 to 7000 yr BP combined with lower C/N ratios suggest a shift to drier conditions. Around 7000 yr BP and 6000 yr BP, $\delta^{13}C$ values decrease at Boston Lake and Copper Falls Lake, respectively. The different

timing of this change could be related disparities in lake-catchment responses to a climate forcing (e.g. residence time, catchment area, topography) or uncertainties in the age-model. For example, Copper Falls Lake is well dated over this interval (Table 3-6), but Boston Lake lacks age-control between the two dates at ~8700 and 4500 yr BP (Table 3-9). From 7000 to 6000 yr BP, both sites record a shift to lower $\delta^{13}C$ and higher C/N ratios, indicate a shift to wetter conditions at both sites. For example, at Boston Lake C/N values increase to values between 20 and 40, indicating the predominate input of organic matter to the core site was from terrestrial sources (Table 4-1). This suggests that transport process to Boston Lake were enhanced during this time, consistent with wetter conditions. Relatively wet conditions remain at both sites for the duration of the Holocene.

In general, a dry early Holocene followed by wetter conditions in the late Holocene is consistent with other paleoclimate records from the region. Previous pollen work from a lake on the Keweenaw Peninsula (i.e. Mud Lake) was compared with the $\delta^{13}C$ records at both Copper Falls and Boston Lake to investigate changes in pollen-inferred vegetation during shifts in $\delta^{13}C$ (Booth, 2002). In general, the early Holocene dry period forests on the Keweenaw Peninsula appear to have been dominated by *Pinus*. A shift to wetter conditions around 6500 yr BP is characterized by a rise in *Betula* and *Tsuga* pollen, which is consistent with a shift to wetter conditions and expansion of wetlands reported in other studies (Booth, 2002; Brugam and Johnson, 1997; Henderson et al., 2010). This general pattern of dry to wet conditions over the Holocene on the Keweenaw Peninsula appear to be the opposite to that found in the southwestern Great Lakes region, which shift to drier conditions from ~6600 to 3200 yr BP (Booth, 2002). This indicates that atmospheric circulation changes associated with the early

Holocene dry period, affected regions differently around the Great Lakes, and may have been related to source changes (Kirby et al., 2002; Yu et al., 1997).

4.4.3 Landscape disturbances from copper mining?

Sorbed Pb concentrations from Copper Falls Lake and Boston Lake were compared with the $\delta^{13}C$, $\delta^{15}N$, and C/N records to investigate the possibility of landscape disturbances from copper mining (Kaushal and Binford, 1999; Meyers, 1997). For example, both lakes record a sudden decline $\delta^{13}C$ in the late 19th century that corresponds with the modern deforestation of the catchment and rise in Pb deposition from smelting and fossil fuel combustion (Kerfoot and Robbins, 1999). Deforestation can lead to soil instability and heightened erosion rates and therefore greater fluxes of nutrients and depleted carbon from soils in the catchment (Kaushal and Binford, 1999; Meyers, 1997). Similarly, a sudden decline in $\delta^{13}C$ occurs at Copper Falls Lake ~5500 yr BP that coincides the maximum sorbed Pb concentrations recorded in the prehistoric record (Figure 4-4-3). However, at Boston Lake the spike in sorbed Pb ~9400 yr BP was not followed by a decline in $\delta^{13}C$, and instead appear to increase following the spike in Pb concentrations (Figure 4-4-3). The lack of a $\delta^{13}C$ decline at Boston Lake suggest that landscape disturbances associated with mining in the catchment during this period were minimal, which is consistent with the Whittlesey map of the ancient mine pits that show mine pits that are located outside the catchment of the lake (Whittlesey, 1862)(Figure 3-3-2). At Copper Falls Lake, the Whittlesey (1862) map indicates that the copper mine pits were likely closer to Copper Falls Lake, which may have led to greater disturbances in the immediate catchment of the lake. However no Cu concentration increases coincide with the increases in Pb detected at both

Copper Falls Lake and Boston Lake in prehistory, except at Boston Lake during in the modern period when waste rock from mining was dumped on the northern shoreline of the lake. Sorbed Cu concentrations have previously been shown to be a proxy of chemical weathering of waste rock associated with copper mining (2.2.4). The lack of any prehistoric Cu concentration increases associated with spikes in Pb and K at Copper Falls and Boston Lake, suggests that the mechanism delivering Pb and K to the sediment was not just a simple process related to weathering waste rock deposited in the catchment. The preferential increases in Pb and K, relative to Cu and lithogenic metals found in the bedrock (Table 2-5, Table 3-12), suggest that the delivery of Pb and K probably included atmospheric sources. This is supported by my observations around the catchment, which indicate that the ancient copper mines noted by Whittlesey (1862) occurred outside the catchment of Boston and Copper Falls Lake.

At Boston Lake, the largest Pb spike occurred during the Early Archaic archeological period, whereas at Copper Falls Lake the highest concentration Pb spike occurred during the Middle Archaic Period (Martin, 1999; Pleger and Stoltman, 2009). A shift in $\delta^{13}C$ ~5500 yr BP following an increase in sorbed Pb at Copper Falls Lake suggest that landscape disturbances were limited to mining that occurred in the Middle Archaic, which would also explain why earlier increases in Pb failed to produce a subsequent shift in $\delta^{13}C$ during the Early Archaic period at both Boston and Copper Falls Lake. The sudden decline in $\delta^{13}C$ ~5500 yr BP at Copper Falls Lake is also coincident with a period of aridity inferred from Elk Lake in southwest Minnesota (Smith et al., 1997; Smith et al., 2002), raising the possibility that the $\delta^{13}C$ aberration could have been related to a climate change event. In conclusion, potential landscape disturbances associated with copper mining appear to be confined to ~5500 yr BP during the Middle Archaic period at Copper Falls Lake. However, without more proxy indicators that are

sensitive to hydroclimate and vegetation changes, the cause of the sudden $\delta^{13}C$ decline following the Pb spike at Copper Falls Lake is still uncertain.

4.5 CONCLUSIONS

The stable isotopes of nitrogen (N) and carbon (C) in organic matter sedimented in Copper Falls and Boston Lake are used to reconstruct Holocene paleoenvironmental change on the Keweenaw Peninsula. Higher C/N and lower $\delta^{13}C$ is interpreted to reflect wetter conditions and enhanced carbon delivery from the watershed, whereas drier conditions occur during the opposite conditions. The $\delta^{13}C$ and C/N records at Copper Falls Lake and Boston Lake, indicate drier conditions from ~10000 to 6500 yr BP, followed by relatively wet conditions from 6500 yr BP to present (Figure 4-4-4). In general, this pattern is consistent with findings from other paleoclimate studies in the region (Booth, 2002; Brugam and Johnson, 1997). Comparisons of the $\delta^{13}C$ and sorbed Pb concentrations from both sites, suggests that landscape disturbances may have been associated with copper mining at Copper Falls Lake ~5500 yr BP. However, the coincidence with climate change events detected at Elk Lake Minnesota (Smith et al., 2002), raise the possibility that the $\delta^{13}C$ aberration may be related to other causes. Thus additional proxy indicators are needed to test the landscape disturbance hypothesis.

5.0 HUMAN IMPACTS FROM CAHOKIA RECORDED IN HORSESHOE LAKE SEDIMENTS

5.1 INTRODUCTION

Cahokia is the largest known population center in the Pre-Columbian United States (Pauketat, 2009; Pauketat and Emerson, 1997). Located on the floodplain of the Mississippi River near modern day East St. Louis, Illinois, archeological evidence suggests that from ~1050 to 1350 AD thousands of people lived at Cahokia and constructed hundreds of earthworks, including Monks Mound, the third largest monumental earthen mound in North America (Figure 5-1)(Pauketat, 2009). The people of Cahokia lived in one of the earliest urban landscapes (Iseminger, 2010; Pauketat, 2009) in the United States and relied on agriculture, including crops such as maize (*Zea Mays*), sunflowers (*Helianthus*), and squash (*Cucurbita*). After ~1200 AD, archeological records suggest that Cahokia fell into decline (Pauketat and Emerson, 1997). The area appears to be sparsely populated by ~1400 AD until European settlement in the region beginning in 1696 AD (Meeks and Anderson, 2013). Cahokia was part of the larger Mississippian Tradition or Southeastern Ceremonial Complex. Settlements associated with the Mississippian Tradition are typically found near rivers and are characterized by the construction of flattop earthen mounds, wooden palisade walls, and leveled plazas (Pauketat and Emerson,

1997). It is unclear to what degree, and over what duration, urbanization at Cahokia influenced the environment (e.g. clearance for fuel and agriculture)(Lawler, 2011; Lopinot and Woods, 1993) and was impacted by climate change (e.g. droughts)(Benson et al., 2009; Meeks and Anderson, 2013).

Previous work suggests that Pre-Columbian societies in North America altered the landscape and composition of vegetation for agriculture and agroforestry (Beach et al., 2009; Munoz et al., 2014a; Rosenmeier et al., 2002). Similarly, prehistoric copper mining activity in the regions surrounding Lake Superior enhanced the delivery and subsequent concentrations of lead, copper, and potassium in lake sediment (2.2.4, 3.4). Here I use sediment geochemistry to reconstruct how Cahokia (a Pre-Columbian city in Illinois, United States) impacted the metal and nitrogen cycles in an adjacent lake.

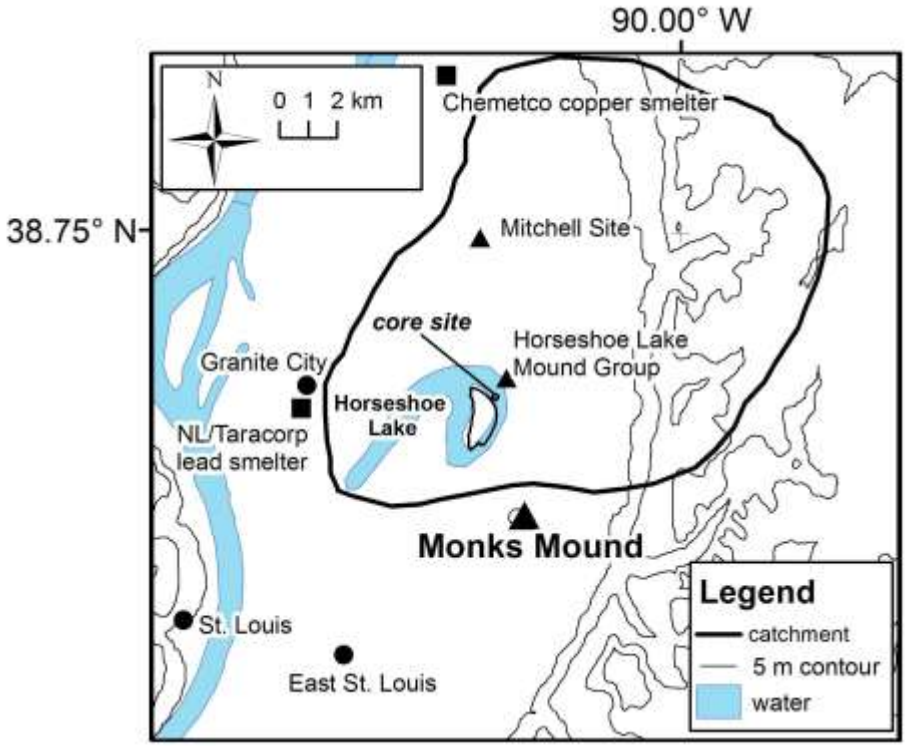


Figure 5-1 Map of the Horseshoe Lake watershed in relation to Cahokia and the NL/Taracorp lead smelter and the Chemetco copper smelter.

I collected sediment cores from Horseshoe Lake, an alkaline oxbow lake located ~3 km north of Monks Mound to address these questions (Figure 5-1). I analyzed the sediment using isotopic, geochemical, and palynological proxies and used radiometric dating (^{210}Pb and ^{14}C) to investigate how past human activity changed local environmental systems. Previous, researchers have cored Horseshoe Lake to reconstruct environmental history and associated human disturbances (Brugam et al., 2003; Munoz et al., 2014b; Ollendorf, 1993; Vermillion et al., 2005). Here I review this past work and present an independent 1500-year ^{210}Pb and Accelerator Mass Spectrometry (AMS) ^{14}C dated sediment record with additional proxy data to expand upon earlier paleolimnological studies from Horseshoe Lake. Fossil maize pollen, sorbed metal concentrations (Pb, Cu, K, Al, Ti, Fe), total nitrogen (N), total organic carbon (C), and nitrogen isotope ratios of organic matter ($\delta^{15}N_{org}$) were analyzed, because these proxies are sensitive to human activity that effects the geochemistry and sedimentology of the lake sediment record (e.g., wood smoke, sewage, erosion, agriculture, etc.).

5.2 METHODS

5.2.1 Setting

Horseshoe is an oxbow lake located in the eastern floodplain of the Mississippi River near present day East St. Louis, Illinois (Figure 5-1). The lake has a maximum depth of about 2 m with a surface area of 10.8 km^2 and a watershed area of 190 km^2. The watershed and basin is located is on top of ~12 m of Pleistocene and Holocene floodplain sediment over sandstone and shale bedrock of the Caseyville Formation. The permeable sand and silt-rich sediments contain

an unconfined aquifer that contributes groundwater to Horseshoe Lake (Grimley et al., 2007). Today the watershed is disturbed from agricultural, industrial, and residential activities.

5.2.2 Fieldwork

Eight overlapping cores were collected in 2012 and 2013 AD from the easternmost basin (38.6983° N, 90.0731° W) of Horseshoe Lake in about 1.3 m of water (Figure 5-1). Core A-12 was recovered using a 5.5-cm diameter piston core with a removable polycarbonate tube to a depth of 1.40 m below the sediment-water interface. The flocculate upper 27 cm of sediment from Core A-12 was extruded in the field at 0.5 cm intervals into Whirl-pak bags. A steel barrel Livingstone corer was used to collect overlapping cores from three adjacent core sites (Core B-12, D-13, and E-13) that consist of a total of seven ~1-m long drives. Core E-13 consists of two overlapping drives that span from 1.52 to 3.41 m below the sediment-water interface. A composite core was developed by splicing together the A-12 surface core and E-13 Livingstone cores using visible stratigraphic markers and magnetic susceptibility profiles (Figure 5-2).

I characterized the physical and chemical characteristics of Horseshoe Lake using a Hach Hydrolab equipped with temperature, dissolved oxygen, and pH sensors. Sulfuric acid titrations were conducted on samples of surface water from each lake using a Hach Digital Titrator to determine alkalinity.

5.2.3 Magnetic susceptibility

Magnetic susceptibility was measured on the split-core surface of all the cores at a 0.2 cm interval at room temperature using a Tamiscan high-resolution surface-scanning sensor connected to a Bartington MS2 susceptibility meter at the University of Pittsburgh, Department of Geology and Planetary Science. This was used to stratigraphically correlate cores to compile a composite depth scale used in the age model (Figure 5-2).

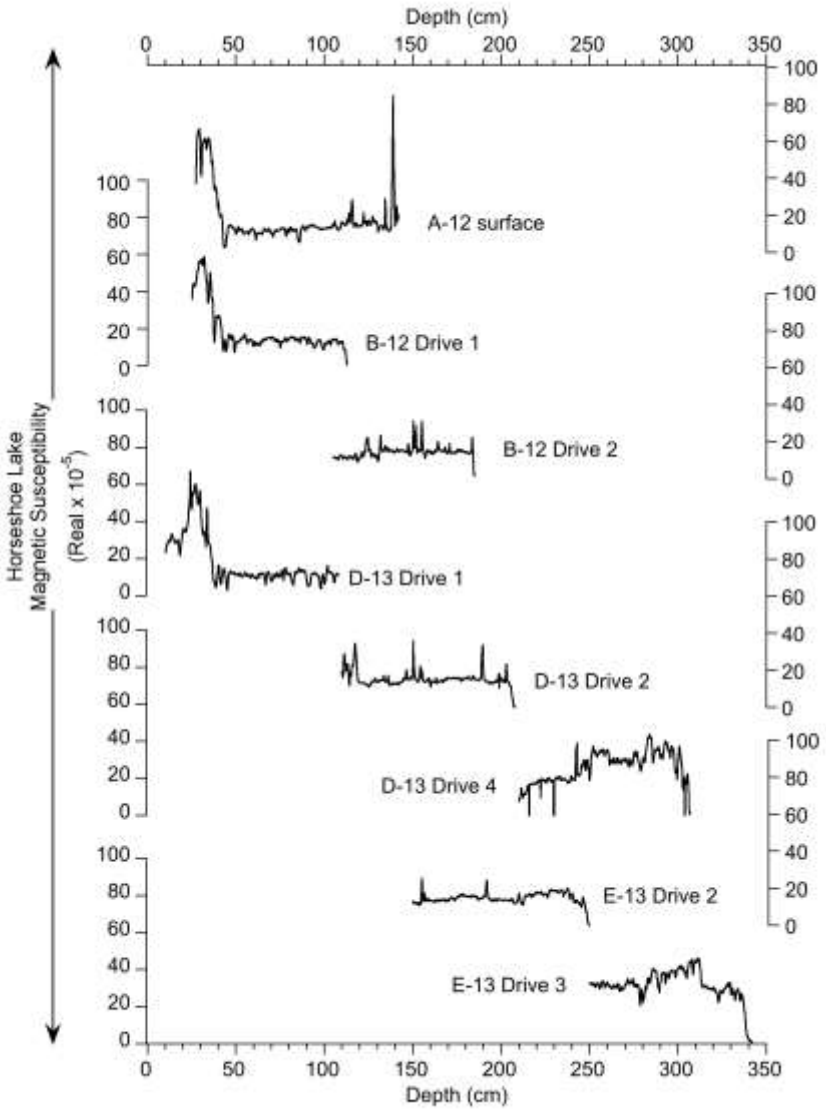


Figure 5-2 Magnetic susceptibility measurments from the Horseshoe Lake sediment cores. Magnetic susceptibility and visual sedimentology were used to compile a composite depth scale.

5.2.4 Geochronology

Eight >125 μm charcoal samples were measured for ^{14}C at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California, Irvine. I selected charcoal for dating because it is typically sourced from burned terrestrial plants, and therefore is

not affected by carbon reservoir effects. Prior to analysis, samples were pretreated using a standard 1 M HCl, 1 M NaOH, 1 M HCl procedure and rinsed in deionized water to a neutral pH (Abbott and Stafford, 1996). A total of 14 samples from the upper 25 cm of extruded sediment from the top of core A-12 were lyophilized, sealed in airtight dishes for three weeks, and measured for ^{210}Pb and ^{214}Pb activities by direct gamma counting for 24 hours in a broad energy germanium detector (Canberra BE-3825) at the University of Pittsburgh's Department of Geology and Planetary Science. The unsupported ^{210}Pb (i.e., ^{210}Pb minus ^{214}Pb) assays were interpreted using the constant rate of supply (CRS) model. The resulting ages were input into CLAM for R to generate an age-model (Blaauw, 2010) using the IntCAL09 calibration curve (Reimer et al., 2009).

5.2.5 Loss-on-ignition

Sediment sub-samples were collected at 2- to 5-cm intervals down Cores A-12 and E-13 using a 1-cm^3 piston sampler and dried for 48 hours at 60 °C to calculate dry bulk density values. Weight percent organic matter and carbonate content of the dried samples was determined by loss-on-ignition (LOI) analysis at 550 °C for four hours and at 1000 °C for two hours, respectively (Heiri et al., 2001).

5.2.6 X-ray diffraction

The mineralogy of the core from was investigated by powder x-ray diffraction (XRD) using a Philips X'Pert X-ray Diffractometer at the University of Pittsburgh Swanson School of Engineering and at the Large Lakes Observatory at the University of Minnesota Duluth. Four 1-

cm-thick samples were taken at a mean depth of 26.0, 41.5, 210.5, and 310.5 cm and pretreated using 7% H_2O_2 for 24 h at room temperature to remove organic matter. The sediments were then washed with deionized water, frozen, lyophilized, and homogenized before XRD analyses. The spectra were analyzed using X'Pert Graphics and Identify and Philips High Score Plus with a phase database from the International Centre for Diffraction Data to identify minerals present.

5.2.7 Maize pollen

A total of 26 sediment sub-samples were analyzed for maize pollen at the Instituto de Geología, Universidad Nacional Autónoma de México. A volume of 0.5 cm^3 was processed following standard protocols for pollen analysis (Faegri and Iversen, 1989) and subsequently sieved through a 50-μm mesh. Samples were scanned at x400 and x1000 magnifications using a transmitted light microscope until maize pollen was found or until the entire sample was examined.

5.2.8 Charcoal analysis

A known volume of sediment was extracted at the Instituto de Geología for charcoal counts from the same sub-samples analyzed for maize pollen. The sediment was disaggregated using sodium pyrophosphate to separate charcoal particles from the sediments. Charcoal particles were manually separated under a stereo microscope at 50x magnification (Clark, 1988). A digital picture of the samples was taken in order to determine the number of pixels and therefore the area of covered by charcoal using ImageJ software (Rasband, 2005). The charcoal area (mm^2) was then normalized to sediment volume (i.e., mm^2/cm^3).

5.2.9 Sorbed metal analysis

Metals were extracted from sediments using 10% HNO_3 and concentrations measured on a Perkin Elmer NeXION 300x Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). This method extracts metals sorbed to exchange sites in sediments and contained in carbonate minerals, in contrast to total metal concentrations derived from analysis of bulk sediment mineral matter (e.g., HF digestions). Sorbed metal concentrations are sensitive to inputs from anthropogenic activity (Graney et al., 1995). Moreover, excavations at Cahokia have revealed a Mississippian-era copper workshop and copper artifacts at the site (Kelly and Brown, 2010), raising the possibility of metal emissions and direct transfer of metal rich materials to the lake.

Metal concentrations were measured at 2- to 5-cm intervals. One interval of interest from 197 to 221 cm was resampled and analyzed at continuous 1-cm intervals. All samples were lyophilized and homogenized prior to analysis. After 24 hours the sediment-acid mix was centrifuged and the resulting supernatant was extracted for metal concentration measurements using a Perkin Elmer NeXION 300x ICP-MS at the University of Pittsburgh, Department of Geology and Planetary Science. The detection limit is <1 μg g^{-1} for lead, copper, potassium, aluminum, and iron. Metals liberated from sediments using 10% HNO_3 are referred to as 'sorbed' in this study. Standards, blanks, and duplicates were measured during the analyses to ensure accuracy and reproducibility.

5.2.10 Nitrogen and carbon analysis

Weight percent nitrogen (N), carbon (C), and nitrogen isotopes of organic matter ($\delta^{15}N_{org}$) were measured on core sub-samples taken at 3- to 5-cm intervals. Samples were treated twice with 1 M HCl for 24 hours to dissolve carbonate minerals and rinsed back to neutral pH with deionized water. Samples were then lyophilized and analyzed at the Environmental Isotope Laboratory at the University of Arizona using a continuous-flow gas-ratio mass spectrometer (Finnigan Delta PlusXL) coupled to an elemental analyzer (Costech). Samples were combusted in the elemental analyzer. Nitrogen isotopes of organic matter are expressed in conventional delta (δ) notation as per mil (‰) and are reported relative to atmospheric N_2. Standardization is based on acetanilide for elemental concentration and IAEA-N-1 and IAEA-N-2 for $\delta^{15}N$. Precision is better than ±0.2‰ for $\delta^{15}N$, based on repeated internal standards.

Table 5-1 Madison County (1878 km^2) census livestock records

Year (AD)	Ungulates	Horses	Asses	Swine	Sheep	Goats	Total livestock	Animal units*
1950	1566	348	2457	2114	173		6658	5616
1940								
1930	30143	9065	3546	33215			75969	53460
1920	31902	13543	4409	29924	3309	59	83146	61438
1910	31105	13621	4393	39198	7090	109	95516	64328
1900	29285	13031	4046	57774	6807	62	111005	66991
1890	24679	14396	4947	65600	6822		116444	67928
1880	15919	12076	4772	62892	9515		105174	56476
1870								
1860	22315	8727	1245	39200	4708		76195	45696

* Animal units provide an indicator of forage consumed by livestock by normalizing for animal species and weight. Animal unit equivalency values are taken from National Range and Pasture Handbook (USDA, 1997).

5.3 RESULTS

5.3.1 Water chemistry

In May 2013 the surface water of Horseshoe Lake had an alkalinity of 114 mg l^{-1}. Measurements of the water column were taken at 10 cm intervals to a depth of 1.3 m. Average water temperature was 19.9° C, dissolved oxygen concentration was 7.6 mg l^{-1}, and the pH was 8.7 (Table 5-2). The water column was mixed and contained an oxygenated sediment-water interface.

Table 5-2 Hydrolab measurements

Water depth (m)	Temperature (°C)	Dissolved oxygen (mg l^{-1})	pH
0.1	19.89	7.90	8.74
0.2	19.93	7.87	8.75
0.3	19.93	7.84	8.78
0.4	19.95	7.83	8.79
0.5	19.94	7.83	8.77
0.6	19.93	7.84	8.77
0.7	19.93	7.83	8.77
0.8	19.92	7.82	8.75
0.9	19.86	7.72	8.72
1.0	19.75	7.49	8.70
1.1	19.74	7.29	8.68
1.2	19.71	7.07	8.67
1.3	19.62	6.66	8.60

5.3.2 Age-model

The age to depth model was generated using eight AMS radiocarbon dates and fourteen CRS ^{210}Pb ages using the Classical Age Modeling Code for R (Blaauw, 2010)(Table 5-3, Table 5-4). A smooth spline (tension=0.8) was used to interpolate between the age constraints and to generate 95% confidence intervals (Figure 5-3). One radiocarbon age was omitted because of an anomalous age in the context of the other seven dates (Figure 5-3). This old age suggests that the macrofossil is contaminated with dead carbon or represents reworked material that does not reflect the true age of deposition. From 450 to 1350 AD (336 to 168 cm depth), the sedimentation rates were 0.19 cm year^{-1} on average. After 1350 AD (168 to 0 cm), average sedimentation rates increased to 0.27 cm year^{-1}.

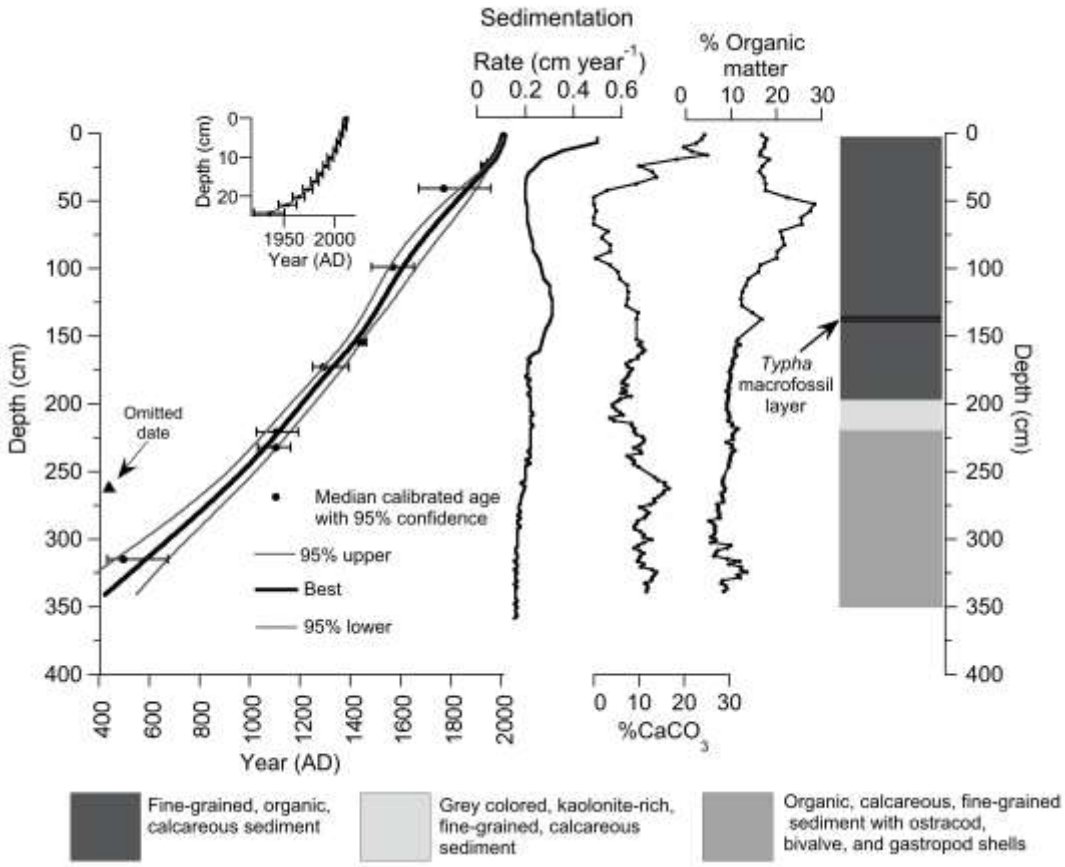


Figure 5-3 (Left to right) Horseshoe Lake age model compared with sedimentation rates, $CaCO_3$, organic matter and a simplified stratigraphic column.

Table 5-3 Horseshoe Lake constant rate of supply (CRS) ^{210}Pb dates

Depth (cm)	Unsupported Pb-210 (Bq g^{-1})	Error (1 sig)	Cum. Wt. Flux (g cm^{-2})	CRS Age (yr AD)	Error (1 sig)
0	0.167	0.024	0.055	2011	2
0.25	0.118	0.018	0.297	2010	2
2.25	0.116	0.017	0.670	2007	2
4.25	0.101	0.017	1.023	2004	2
6.25	0.102	0.015	1.433	2001	2
8.25	0.128	0.016	1.844	1996	3
10.25	0.103	0.015	2.278	1992	3
12.25	0.106	0.014	2.724	1986	3
14.25	0.089	0.014	3.151	1981	4

16.25	0.090	0.014	3.587	1974	5
18.25	0.089	0.013	4.076	1965	6
20.25	0.053	0.010	4.734	1954	9
22.25	0.058	0.008	5.410	1936	15
24.25	0.060	0.018	6.265		

Table 5-4 Horseshoe Lake ^{14}C dates

UCIAMS #	Depth (cm)	^{14}C year B.P.	Error (σ)	Calendar (yr AD[1])	Error (95% upper)	Error (95% lower)
109369	39.5	165	20	1764	1952	1666
109370	97.5	315	35	1562	1648	1479
141370	153	450	20	1441	1457	1424
116877	171.5	705	35	1285	1389	1244
141371	219.5	935	40	1099	1186	1021
141372	231	945	30	1096	1156	1025
141373*	257	1620	15	418	532	392
131498	313.5	1460	70	490	669	427

*Date omitted from the age-model.
[1]This is the median of the 95% calibration (CALIB 6.0) distribution (Stuiver et al., 2010).

5.3.3 Sedimentology

This study focuses on cores recovered from the eastern basin of the lake indicated in Figure 5-1. At this site, sediment was deposited continuously over the last 1500 years and does not contain evidence of unconformities or desiccation features (Figure 5-3). Overall the sediment is fine-grained (clay to silt), calcareous, visibly homogeneous, and contains shells from freshwater gastropods, bivalves, and ostracods. A 1 cm layer deposited around 1480 AD contains abundant *Typha* macrofossil remains. The exception to the homogenous layering occurs

with the deposition of a distinct silt -rich gray colored layer (Figure 5-3) about ~20 cm thick that is dated (±95% confidence) from 1150±50 (197 cm) to 1220±50 AD (221 cm).

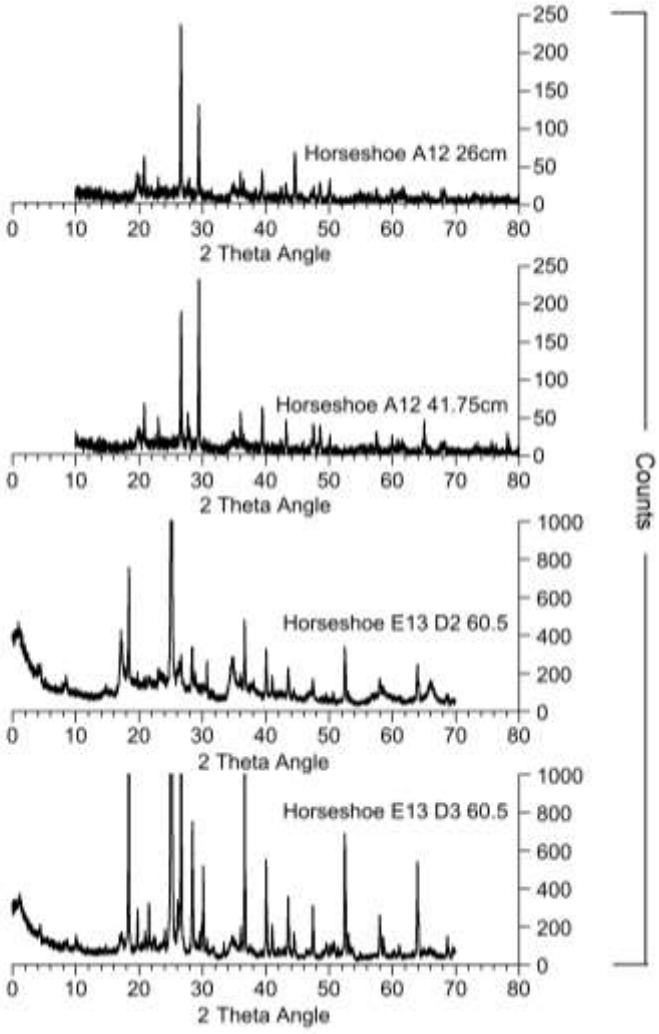


Figure 5-4 X-ray diffraction (XRD) data from Horseshoe Lake sediments

XRD samples were taken from sediment depths dated to 610, 1160, 1860 and 1940 AD (26, 42, 211, and 311 cm). All of the samples contained quartz and calcite. The samples from 1160 and 1860 AD included muscovite, while samples from 610 and 1160 AD contained anorthite minerals. The sample from 1160 AD differs from all the other samples with respect to mineralogy in that it contains kaolinite (Figure 5-4).

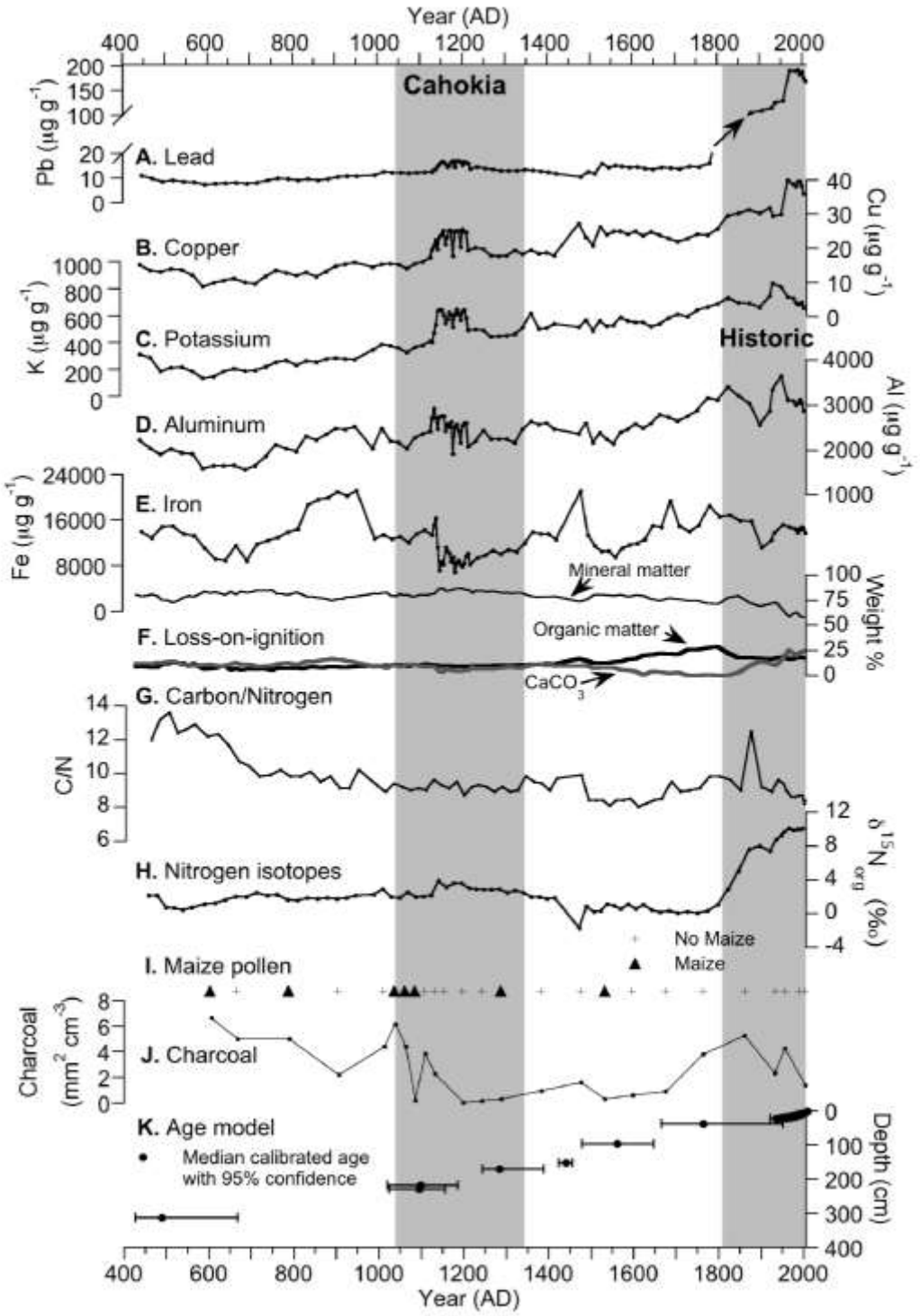


Figure 5-5 Sorbed metal concentrations (A-E), loss-on-ignition (F), carbon/nitrogen (G), nitrogen isotopes (H), maize pollen (I), charcoal (J), and radiometric constraints used in the age model (K).

5.3.4 Woodland Period: 450 to 1050 AD

In the oldest sediment analyzed, lead, copper, potassium, and aluminum concentrations are low and stable, at respective average concentrations of ~10, 13, 245, 2040 μg g^{-1}. Iron is at relatively low average concentrations of ~12700 μg g^{-1} from 450 to 800 AD, the increases to ~17500 μg g^{-1} from 800 to 1050 AD. Sediments are composed of ~8% organic matter, 12% $CaCO_3$, and 80% residual mineral matter. Carbon/nitrogen ratios (C/N) average 13 from ~450 to 650 AD, and gradually decrease to a value of 9 by 1050 AD. Nitrogen isotopes are low and stable during this with average values of 1.7‰. Charcoal is at relatively high between 2 to 7 mm^2 cm^{-3} with the highest amount of particles from sediments dated to 610 and 1040 AD. Maize pollen is found in three of the six samples dated to 610, 790, and 1040 AD (Figure 5-5).

5.3.5 Mississippian Period: 1050 to 1350 AD

From ~1050 to 1150 AD, lead, copper, potassium, and aluminum remain similar to concentrations from 450 to 800 AD. Starting at 1150 AD, copper, potassium, and aluminum rise to respective values of ~25, 600, and 3000 μg g^{-1} and remain at elevated concentrations until 1220 AD, while iron and charcoal concentrations decrease to ~10,000 μg g^{-1} and 1.1 mm^2/cm^3 (Figure 5-6). After 1220 AD, copper, potassium, aluminum, and iron shift to lower concentrations in the sediments. Similarly starting around 1150 AD, $\delta^{15}N_{org}$ shifts to higher values (3.9‰), and remains elevated until ~1300 AD, while charcoal is at relatively low concentrations. Carbon/nitrogen ratios, organic matter, $CaCO_3$, and mineral matter change little from 1150 to 1350 AD, suggesting minimal overall changes in bulk sediment composition.

Maize pollen is observed in three of the eight samples dated to 1070, 1090, and 1290 AD (Figure 5-5).

5.3.6 Vacant Quarter: 1350 to 1808 AD

Lead remains at stable and low concentrations, while copper, potassium, and iron concentrations gradually increase over this interval. A sudden increase in copper ~1480 AD corresponds with a 1-cm thick layer rich in *Typha* macrofossils (Figs. 2 & 3), a 2‰ decrease in $\delta^{15}N_{org}$, an increase in iron concentrations (~21000 μg g^{-1}), and slightly higher C/N values (~10). Other than this layer, $\delta^{15}N_{org}$ and C/N values remain at stable values while LOI records a trend to higher organic matter concentrations ~28% with corresponding shifts to lower mineral matter and $CaCO_3$ concentrations. Charcoal remains at low concentrations from 1350 AD to 1700 AD (<2 mm^2 cm^{-3}) until shifting to higher concentrations by 1770 AD. Aluminum concentrations remain stable until increasing around 1750 AD. Maize pollen is only detected in one out of six samples dated to 1540 AD (Figure 5-5).

5.3.7 Historic Period: 1808 to 2012 AD

The outstanding features of this interval include a spike in C/N to 12.5 at 1880 AD and an increase in both Pb and $\delta^{15}N_{org}$ to values about ten-times the average concentrations deposited during the previous ~1500 years (15 μg g^{-1} and ~1‰, respectively). Copper concentrations increase to about 10 μg g^{-1} from 1950 to 1970 AD, while potassium concentrations remain stable

(Figure 5-6). Charcoal and aluminum concentrations are variable, but elevated. From 1860 to 2009 AD, charcoal concentrations decrease to 1.3 mm^2/cm^3 and $CaCO_3$ concentrations increase to 24%. Iron remains stable and slowly decreases through time to ~14,200 $\mu g\ g^{-1}$ (Figure 5-5). Interestingly, none of the five samples analyzed show evidence for maize pollen, even though historical records and field observations indicate that cornfields existed around the lake during the modern period.

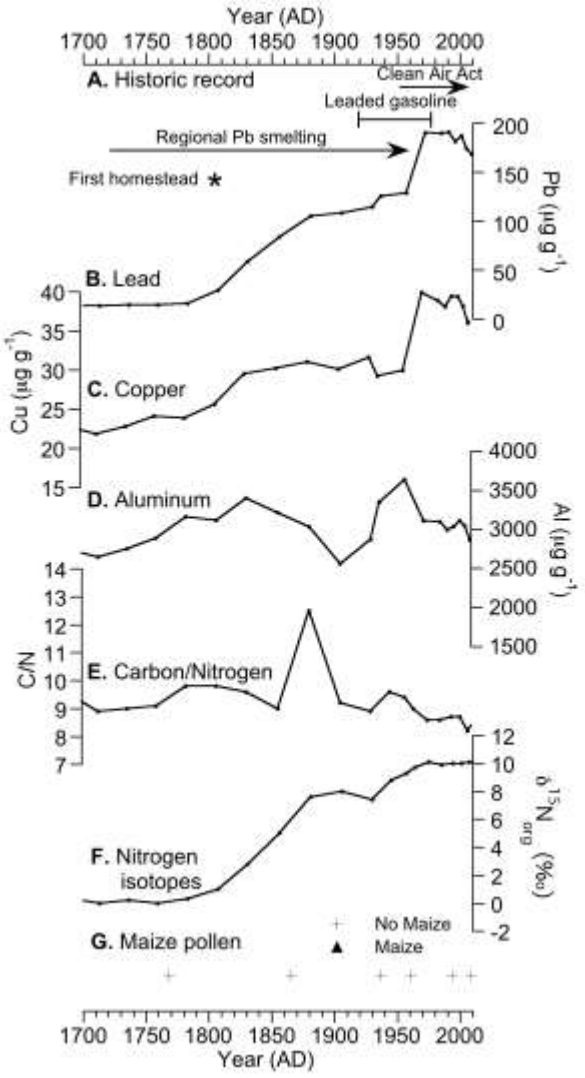


Figure 5-6 Historic events timelime (A) compared against the sorbed metal proxies (B-D), C/N (E), nitrogen isotopes (F), and maize pollen (G) from 1700 to 2010 AD.

5.4 DISCUSSION

5.4.1 Core Stratigraphy

The sediments are fine-grained, homogenous, dark gray-brown, with the exception of a distinct gray layer deposited from ~1150 to 1220 AD (Figure 5-3) that I interpret to have formed as a result of watershed disturbances during the peak in human population and earthen mound construction at Cahokia. Previous sedimentological work at Horseshoe Lake by Munoz et al. (2014b) interpreted this layer as a flood deposit based on a radiocarbon date reversal, the presence of a similar layer in cores recovered from other areas in the basin, and low pollen concentrations. Other recent work found a similar layer in sediment cores recovered from a comparable oxbow lake (i.e., Grassy Lake) located near Mississippian-era settlements (e.g., Dogtooth Bend) 200 km south of Horseshoe Lake (Munoz et al., 2014c). Flood deposits are likely preserved throughout the 1500-year long sediment core at Horseshoe Lake because it is located in the modern 100-year floodplain of the Mississippi River (FEMA, 1976) and was flooded several times (e.g., 1785, 1844 AD, etc.) prior to the construction of the levees in the area (NOAA, 2014). Despite being flooded before levees, there is no evidence for individual floods in the sediment record over the last 1000 years using the proxies in this study (Figure 5-5). This suggests that sorbed lead, copper, potassium, aluminum, LOI, and $\delta^{15}N_{org}$ remain relatively stable in the sediments during flooding events. The high frequency of flooding prior to the construction of levees, combined with high sedimentation rates, and sediment mixing, may make it hard to resolve any single flood event. In addition, the thickness of a flood deposit in a lake is not necessarily proportional to flood magnitude through time. Flood magnitude includes a combination of variables such as stage, velocity, and duration, and is affected by changing

channel morphology. For example, high flow velocities could lead to an erosive or non-depositional setting in the lake basin. Therefore layer thickness as a record of flood magnitude in floodplain lakes must be demonstrated on a site specific basis which was not discussed by Munoz et al. (2014b). Furthermore, the four radiocarbon dates constraining the top and bottom of this layer presented in this study do not suggest instantaneous deposition (Figure 5-3, Table 5-4). Likewise, the presence of a distinctive sediment layer deposited around the same time at Grassy Lake (Munoz et al., 2014c) does not necessarily imply a flood either, because the lake is also near Mississippian-era settlements, such as Dogtooth Bend. For instance, this layer might indicate that the landscape disturbances associated with Mississippian settlements were widespread, similar to the so-called Maya Clay layer(s) in lakes near Preclassic and Classic Maya settlements found over a relatively large geographical area (Anselmetti et al., 2007; Brenner et al., 2002; Rosenmeier et al., 2002). Additionally, similar layers have been reported in lakes with watersheds that were altered for rice agriculture in China (Hillman et al., 2014), and in lakes that receive drainage from ancient copper mines on Isle Royale in Lake Superior (2.2.3.2).

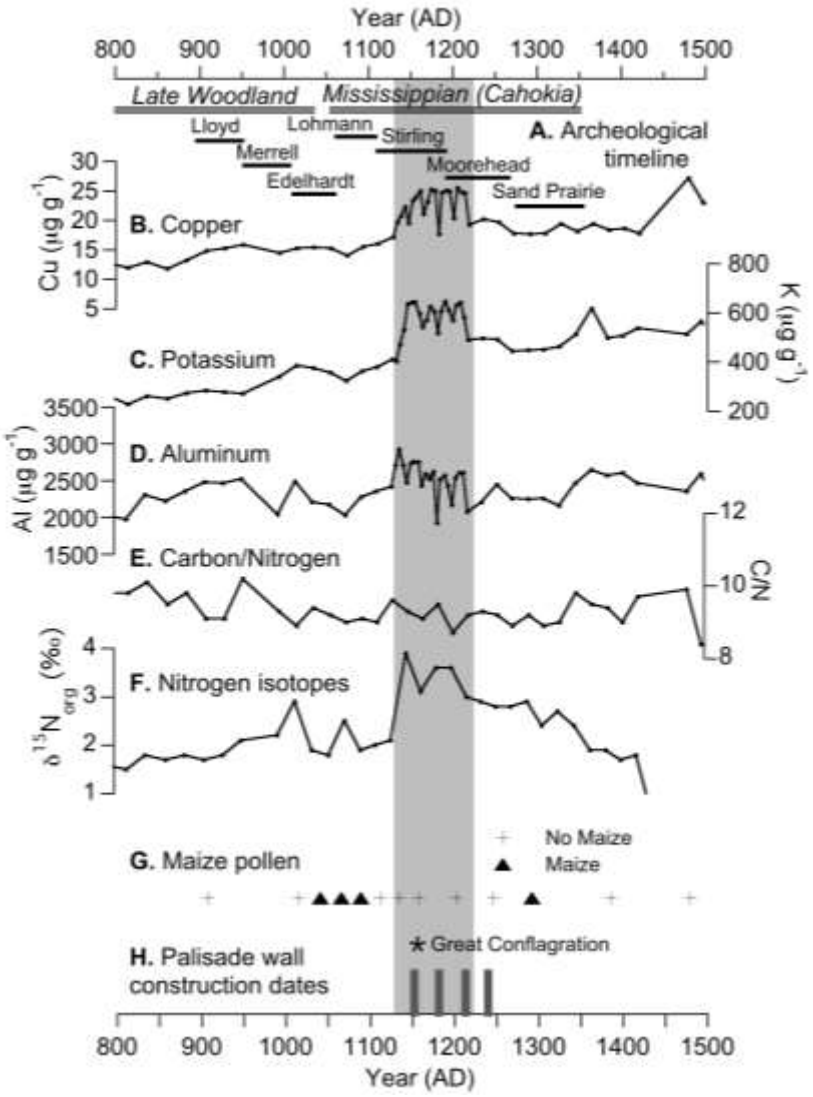


Figure 5-7 Proxy results from 800 to 1500 AD. The archeological record (A) compared against sorbed copper concentrations (B), potassium (C), aluminum concentrations (D), C/N (E), nitrogen isotopes (F), maize pollen (G), and archeological events, such as the building of the palisade walls (Iseminger et al., 1990) and the so-called Great Conflagration (Pauketat et al., 2013)(H).

5.4.2 Maize pollen

Maize pollen was identified in 7 of the 25 sediment samples analyzed from Horseshoe Lake, specifically in samples from 610 and 790 AD (Figure 5-5). This early date for maize

pollen is broadly consistent with nearby radiocarbon dates of maize remains recovered ~4 km east of Horseshoe Lake, which indicate the presence of maize in the area since at least ~100 BC (Riley et al., 1994). The three sediment samples analyzed from the Lohmann Phase (i.e., 1040, 1070, and 1090 AD) all have maize pollen. The five samples analyzed from Stirling and Moorehead Phases dated from between 1100 to 1250 AD do not contain maize pollen. Maize is detected in one sample from the beginning of the Sand Prairie Phase around 1290 AD and near the end of the *Vacant Quarter* in 1540 AD (Figure 5-5). Interestingly no maize is found from modern samples taken from 1870, 1937, 1961, 1994, and 2009 AD even though it is known that maize was growing around the lake during these times (Figure 5-6). The poor correspondence with the historic record suggests that maize pollen is not a reliable indicator of agriculture occurring in the watershed and therefore is probably not an accurate indicator of maize production in prehistoric times either. Perhaps this is because the concentration of maize pollen to Horseshoe Lake is below detectable concentrations in most areas of the sediment core using current techniques (Faegri and Iversen, 1989; Lane et al., 2010).

5.4.3 Macroscopic charcoal data

Charcoal was counted from the same sediment intervals that were analyzed for maize pollen. Charcoal concentrations were high and variable from 600 to 1200 AD and low and stable from 1200 to 1700 AD before increasing again after 1700 AD. Higher fluxes of charcoal recorded from 600 to 1200 AD could be related to fires started by humans to clear the forests for agriculture or settlements. Similarly, the reduction in charcoal inputs from 1200 to 1700 AD could be related to human-induced burning strategies (e.g., small scale burning of underbrush) (Munoz et al., 2014a) or potentially the gradual depopulation of Cahokia after the Sand Prairie

phase. Following the settlement of the French in 1696 AD, charcoal again increases and remains variable, but high, until present (Figure 5-5). However, inferring human-activities based on macroscopic charcoal alone is challenging because changing charcoal particle concentrations could be naturally mediated by changes in vegetation and climate. For example, changing charcoal-inferred fire regimes broadly correspond with the timing of the Medieval Climate Anomaly (900 to 1200 AD) and the Little Ice Age (1400 to 1800 AD), when global climate appears to have reorganized (Mann et al., 2009; Steinman et al., 2014). Therefore when charcoal alone is used as an indicator of human activities it is hard to determine the extent to which human or natural processes are driving changing fluxes.

5.4.4 Metal concentrations

Sorbed metal concentrations in Horseshoe Lake increase after ~1800 AD. These increases are anomalous compared to sediments deposited between ~450 AD and ~1800 AD (Figure 5-6). Recent increase in lead were likely the result of smelting of lead ores, starting around 1720 AD during French colonial times at Mine La Motte in Missouri (March, 1967), followed by a shift to the St. Louis area, starting with Niedringhaus Steel in 1865 AD (Vermillion et al., 2005). Smelting operations continued around the lake for the first half of the 20^{th} century. Abrupt increases in lead concentrations started again around 1950 AD. This increase is likely a combined effect of the widespread use of tetra-ethyl leaded gasoline starting in the 1921 AD and growth of the National Lead Industry/Taracorp Smelter (Figure 5-1) starting in 1903 AD (Vermillion et al., 2005). The early rise in lead is followed by a spike in C/N and a rise in $CaCO_3$ concentrations around 1880 AD, which coincides with the settling of the first post-

European settlement homesteads around the lake and the peak in livestock populations in Madison County (Table 5-1)(Anonymous, 1882). During this period sorbed copper and potassium concentrations also rise, while aluminum and iron concentrations and variability increase. The increase in sorbed copper concentration around 1970 AD corresponds with opening of Chemetco copper smelter near Harford, IL in 1969 AD (Figure 5-1)(EPA, 2014). Following the closures of the nearby lead smelter in 1983 AD (EPA, 2012), the removal of lead in gasoline (Kovarik, 2005), and the closure of Chemetco smelter in 2001 AD (EPA, 2014), concentrations of both lead and copper decline, but remain at relatively high concentrations (Figure 5-6).

Prior to ~1800 AD, lead, copper, potassium, and C/N ratios remain at low and stable values, except from ~1150 to 1220 AD, when aluminum, copper, and potassium concentrations increase, while C/N ratio remains unchanged. The change in sorbed aluminum concentrations in the sediments is likely related to the delivery of aluminum rich compounds associated with eroding clays, such as kaolinite (i.e., $Al_2Si_2O_5(OH)_4$). This explains why the sample analyzed from ~1160 AD is the only sample that contains kaolinite based on XRD measurements (Figure 5-4). Changing sources of inorganic sediment to the lake was probably caused by one or some combination of the construction of earthen mounds in the watershed (some near the shoreline, Figure 5-1) or erosion from agricultural fields and settlements. However, the steady C/N ratios during this period and minimal change in LOI (Figure 5-5) suggests that human alteration of the watershed in prehistoric times was of a different character than modern times.

Table 5-5 Horseshoe Lake proxy correlation coefficient table

[1]	Pb	K	Cu	Al	Fe	N %	C %	C/N	$\delta^{15}N$ ‰	OM %	$CaCO_3$ %	Mineral Matter %
Pb	1.0	0.6	**0.8**	0.6	0.2*	**0.7**	**0.7**	-0.2	**0.9**	0.4	0.6	**-0.8**
K		1.0	**0.9**	**0.8**	-0.1*	0.5	0.4	-0.6	0.5	0.6	-0.1*	-0.3
Cu			1.0	**0.8**	0.0*	**0.7**	0.6	-0.5	**0.7**	0.6	0.2*	-0.6
Al				1.0	0.3	0.6	0.6	-0.4	0.5	**0.7**	0.0*	-0.5
Fe					1.0	0.5	0.5	0.2*	-0.1*	0.4	0.3	-0.5
N %						1.0	**1.0**	-0.2*	0.4	**0.9**	0.2*	**-0.9**
C %							1.0	0.0*	0.4	**0.9**	0.2	**-0.8**
C/N								1.0	-0.2	-0.2	0.1*	0.0*
$\delta^{15}N$ ‰									1.0	0.1*	0.6	-0.6
OM %										1.0	-0.2*	-0.6
$CaCO_3$ %											1.0	**-0.7**
Mineral Matter %												1.0

*p>0.05

[1]Strongly correlated proxies are defined here as an r-value ≥0.7 highlighted in bold. In general, proxies that are sensitive to anthropogenic activities (lead (Pb), potassium (K), copper (Cu), aluminum (Al), carbon (C), nitrogen (N), $\delta^{15}N$) are strongly correlated with one another. Organic matter (OM) is positively correlated with carbon (C) and nitrogen (N), which are all negatively correlated with mineral matter concentrations. Iron (Fe), C/N, and $CaCO_3$ are not strongly correlated with any other proxy data.

The excavation of a copper workshop at Cahokia dated to ~1200 AD (Kelly and Brown, 2010; Kelly et al., 2009) and the elaborate Mississippian copper artifacts recovered at the site raise the possibility that airborne metal pollution could contribute to increased metal concentrations measured in lake sediments. Copper metalworking would explain why the only sustained prehistoric rise in sorbed copper concentrations after 450 AD occurred from 1150 to 1220 AD. For example, aluminum concentrations increase prior to copper concentrations, and decline from ~1180 to 1220 AD, while copper concentrations remain high (Figure 5-7). This implies that separate geochemical processes are driving the observed changes in copper and aluminum concentrations. Additionally, the rise in copper concentrations occur in the absence of changes in C/N ratios and LOI, which supports the idea that the copper inputs to Horseshoe Lake were related to copper metalworking, because delivery of metals from airborne sources would

have little effect on the bulk organic properties of the sediment (Figure 5-5). Furthermore, the rise in copper co-occurs with a rise in potassium (Table 5-5). Potassium has been used as a proxy for biomass burning in sediment (2.2.4) and ice cores (Eichler et al., 2009; Kehrwald et al., 2012), because burning biomass, such as wood, releases potassium to the atmosphere (Calloway et al., 1989; Fine et al., 2001; Harrison et al., 2012; Kleeman et al., 1999; Larson and Koenig, 1994; Misra et al., 1993; Song et al., 2005). The coinciding increases in copper and potassium concentrations seems reasonable when considering the large populations at Cahokia that would have burned wood or other biomass per year for cooking, heating, and copper metalworking. When wood is burned the majority of the mass is removed from the fire through airborne transport in the form of fly ash, aerosol particulates (e.g. levoglucosan, polycyclic aromatic hydrocarbons, metals, etc.), and gases (e.g. H_2O, CO_2, etc.) that are distributed in the troposphere by wind and deposited on the landscape (Denis et al., 2012; Fine et al., 2001; Kehrwald et al., 2012; Larson and Koenig, 1994; Misra et al., 1993). Since the majority of wood smoke emissions are <63 μm in size (Kleeman et al., 1999) they would be below detection in traditional charcoal analysis, which typically focus on fly ash ≥63 μm. This would explain why charcoal counts do not increase when copper and potassium concentrations increase (Figure 5-5) because emissions likely consisted of mostly fine particles as opposed to coarser fly ash. In addition, copper was likely worked using fires and rock hammers in a process known as annealing (Chastain et al., 2011; Peterson, 2003). Overall, increases in both potassium and copper from ~1150 to 1220 AD suggest that emissions related to one or some combination of wood smoke and copper metalworking are detectable during the Stirling and Moorehead Phases (Figure 5-7).

5.4.5 Nitrogen Isotopes

Lake sediment $\delta^{15}N$ reflects biotic transformations associated with reactive nitrogen cycling, while potentially retaining a signature of source nitrogen-isotopic composition (Wolfe et al., 2013). After about ~1810 AD $\delta^{15}N_{org}$ values in Horseshoe Lake sediments increase until present. These changes in isotopic composition are correlated with human populations recorded in census records from townships surrounding the lake (Table 5-6, Figure 5-8). Therefore the increase in $\delta^{15}N_{org}$ was likely related to changes in the sources and processes affecting the isotopic composition of nitrogen deposited in the lake, which include inputs from dissolved nitrogen in groundwater from sewage (Aravena et al., 1993; Elliott and Brush, 2006), airborne nitrogen deposition from burning biomass and fossil fuels (Elliott et al., 2009; Felix and Elliott, 2013; Redling et al., 2013), nitrogen from fertilizer (Dumont et al., 2005), and manure (Table 5-1)(Widory et al., 2005). Furthermore, the processes affecting the transport of nitrogen to Horseshoe Lake could potentially change $\delta^{15}N_{org}$ depending on precipitation, temperature (Craine et al., 2009), agricultural land cover, nitrogen fertilizer application rate (Dumont et al., 2005), soil type, biological communities, and irrigation activities (Evans, 2007; Hodell and Schelske, 1998), among other factors. In addition, nitrogen is fractionated by organisms before, during, and after sedimentation (Elliott and Brush, 2006).

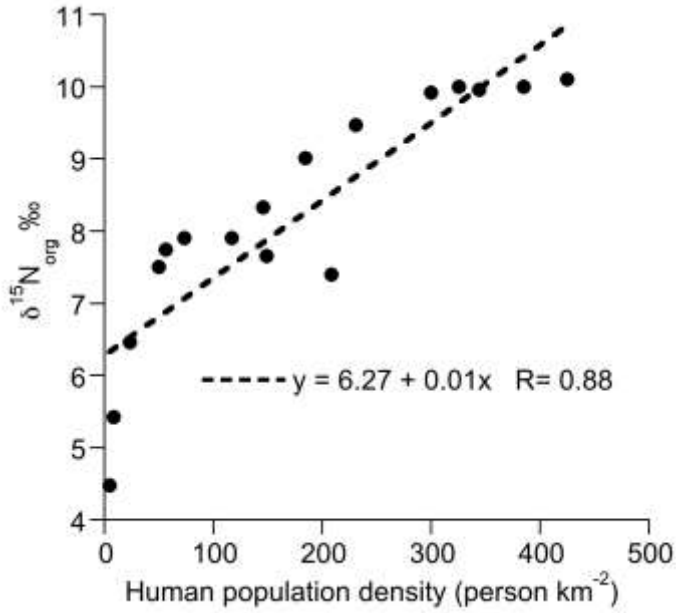


Figure 5-8 Linear regression between nitrogen isotopes and human populations taken from census records from 1850 to 2010 AD.

Table 5-6 United States Census records of human populations

Year (AD)	Chouteau 77 km²	Edwardsville 51 km²	Collinsville 38 km²	Nameoki 57 km²	Total population	Population per km²
2010	8226	37657	36265	12685	94833	425.26
2000	8010	33731	32954	11186	85881	385.12
1990	7792	26665	29842	12492	76791	344.35
1980	8627	23249	27158	13606	72640	325.74
1970	8521	18166	26373	13872	66932	300.14
1960	6194	15975	20122	9210	51501	230.95
1950	3458	13459	15082	9230	41229	184.88
1940	2311	11194	12311	6669	32485	145.67
1930	1391	11252	12084	21817	46544	208.72
1920	818	9281	12084	11110	33293	149.30
1910	768	8705	10607	6050	26130	117.17
1900	875	6907	5812	2834	16428	73.67
1890	954	4844	5224	1558	12580	56.41
1880	1004	4133	4577	1466	11180	50.13
1870		2193			2193	9.83
1860		53			53	0.24
1850		677			677	3.04

From ~1350 to 1800 AD, the $\delta^{15}N_{org}$ record is stable, averaging 0.6 ± 0.8‰ (μ±σ). Around 1150 AD there is a distinct increase to 3.9‰. Higher average $\delta^{15}N_{org}$ values (3.0 ± 0.5‰) are recorded until 1350 AD. Prior to 1150 AD, $\delta^{15}N_{org}$ is more variable but at low values of 1.7 ± 1.7‰. Higher $\delta^{15}N_{org}$ values from 1150 to 1350 AD coincide with the Stirling, Moorehead, and Sand Prairie Phases, when the archeological record indicates Cahokia was densely populated (Pauketat and Emerson, 1997). Therefore I suggest that the increase in $\delta^{15}N_{org}$ was likely related to some combination of changes in the sources and processes affecting the $\delta^{15}N_{org}$ of lake sediment, including reactive nitrogen from sewage seepage in midden pits, reactive nitrogen inputs from disturbed soils, and airborne deposition of nitrogen from wood smoke. For example, landscape disturbances and growing *Leguminosae* (beans) probably led to enhanced inputs of reactive nitrogen and nutrients from soils (Evans, 2007; Meyers, 1997). In addition wood smoke emissions contain nitrogen oxide vapors (Larson and Koenig, 1994), however the nitrogen isotopic composition of wood smoke and other biomass is poorly constrained and appears to vary widely. For instance, the isotopic composition of reactive nitrogen emissions from burning spruce wood has been reported to be around -8‰, whereas the nitrogen isotopic composition of organic hay is as high 12‰, with other sources of biomass falling between somewhere between (Hastings and Fibiger, 2013). Empirical measurements indicate that 0.2 to 0.9 g of nitrogen oxide vapors are emitted when 1 kg of wood is burned (Larson and Koenig, 1994). If I assume wood burned at Cahokia emitted 0.5 g kg^{-1} of nitrogen oxides, then burning 100,000 kg of wood would generate 50 kg of nitrogen oxide vapors, not accounting for the rate of burning and nitrogen lost before being sedimented in the lake. In comparison, if 10,000 people inhabited Cahokia, they would generate between 36,000 to 78,000 kg of nitrogen in sewage per year based on modern empirical measurements (Castro et al., 2003;

EPA, 2002). Thus nitrogen deposition to Horseshoe Lake from biomass emissions was likely small in comparison to the larger nitrogen inputs from sewage. Therefore I presume wood burning would have an insignificant impact on the overall isotopic composition of nitrogen in the lake sediment.

Nitrogen isotopes increase along with potassium and copper concentrations ~1150 AD, suggesting that the same processes were driving these changes. For example, sewage contains potassium (Wen et al., 1997). However this is not entirely supported by the data because potassium and copper decline to background concentrations before ~1220 AD, while $\delta^{15}N_{org}$ decreases more gradually, shifting ~-1‰ from 1300 to 1350 AD. In addition, increases in $\delta^{15}N_{org}$ after ~1810 AD are not tracked by subsequent increases in copper and potassium concentrations (Figure 5-5). Together, this suggests that the processes driving the nitrogen isotopes and metals are different, which supports the interpretation that potassium and copper inputs to the lake were predominately sourced from the airborne fallout of particles, while nitrogen was mainly delivered dissolved in groundwater.

Droughts inferred from tree rings cannot be used to explain the anomalous increases in $\delta^{15}N_{org}$ and sorbed metals from 1150 to 1350 AD in the absence of humans. For example, the increase in $\delta^{15}N_{org}$ partially coincides with a period of heightened aridity detected in tree-ring inferred Palmer Drought Severity Index reconstructions (Cook et al., 2007) described in Benson et al. (2009). The coincidence with drier conditions during this time could imply that aridity caused $\delta^{15}N_{org}$ to increase in the sediments because decreasing precipitation and higher temperatures have been shown to increase both soil and foliar $\delta^{15}N$ (Amundson et al., 2003; Craine et al., 2009). However this relationship only holds, in part, across the period of aridity detected in tree-rings from 1100 to 1245 AD. For example, several other periods of aridity, such

as around 1450 to 1560 AD, fail to produce resulting increases in $\delta^{15}N_{org}$. Although, it is possible that from 1100 to 1245 AD the combination of human activity and drought worked together to effect the lake in ways that may have been different after the region was depopulated following ~1400 AD. Still, recent trends in $\delta^{15}N_{org}$ cannot be explained by changing hydroclimatic conditions and are likely the result of human activities.

5.5 CONCLUSION

Sediments deposited over the last 1500 years at Horseshoe Lake were analyzed to document human-environmental changes associated with the growth and decline of Cahokia, the largest known Pre-Columbian city in the United States. The sediments in Horseshoe Lake reveal that distinct physical, geochemical, and isotopic changes consistent with human impacts can be detected from ~1150 to 1300 yr AD and after 1808 AD when Europeans settled the watershed (Anonymous, 1882). These changes appear to occur independent of natural factors such as flooding or droughts, and coincide with the peak in human population at Cahokia (Pauketat and Emerson, 1997) and construction of a copper workshop ~1200 AD (Kelly and Brown, 2010). Macroscopic charcoal particles and pollen, such as *Zea Mays*, counted in sediment are not able to detect the changes indicated by sorbed metals, nitrogen isotopes, and the archeological record, because domestic wood smoke emissions consist mainly of particulates and gases <63 μm in size (Kleeman et al., 1999), and because the transport and flux of maize pollen to the sediments is likely not a reliable indicator of human impacts to lakes (Lane et al., 2010). This highlights the

need to look beyond charcoal and pollen as ways to document anthropogenic activity around lakes in North America. Other proxies such as sorbed metal concentrations presented here, are sensitive to human activity (Graney et al., 1995) and therefore can be used to inform our understanding of the timing, magnitude, and processes by which human activities associated with Cahokia influenced the Horseshoe Lake. These data can be compared against regional paleoclimate proxies to evaluate the temporal correspondence between climate change and human activity to determine if climate, such as droughts, led to discernable changes in human activity inferred from the sedimentary and archeological record. This represents a shift from viewing lakes as just a source of paleoenvironmental information that can be compared against the archeological record, but rather as a source of anthropogenic data itself.

6.0 CONCLUSIONS

Human-related changes to lakes over the Holocene can be detected in lake sediment records from the Michigan Copper Districts and near Cahokia in Illinois, the largest known Mississippian-era city in the Pre-Columbian United States. The geochemical records presented here provide a new perspective for interpreting Pre-Columbian human history in the United States and can be used to understand how past societies impacted the environment. These data will facilitate comparisons between archeological data and paleoclimate records at a level of temporal precision not possible using artifact deposits alone.

6.1 MICHIGAN COPPER DISTRICTS

Mining and copper use in North America represents one of the oldest examples of metalworking in world prehistory. Native copper was mined from shallow bedrock pits and annealed or heated with fire to aid in extraction and processing (Martin, 1999; Pleger and Stoltman, 2009). Since the early discoveries of prehistoric copper artifacts and mining on the Keweenaw Peninsula in the 19th century (Foster and Whitney, 1850; Hill, 1847), copper metalworking in North America has remained a subject of considerable interest and debate, in part, because copper artifacts were produced starting as early as 8,000 to 9,000 years ago (Libby,

1954; Martin, 1993; Pleger, 2001), during a period that preceded the regional development of agriculture (Smith, 2011). The immense quantities of hammerstones and mine tailing piles found nearly continuously for ~100 km along the elevated ridge within the Keweenaw Peninsula suggest that substantial ecological changes were likely associated with prehistoric copper mining (Whittlesey, 1862). In 1863 AD, Michigan State Geologist Charles Whittlesey said that "[The miners] must have been numerous, industrious and persevering and have occupied the country a long time (Whittlesey, 1863)." This was based on his observation that nearly every accessible native copper deposit showed evidence of prehistoric workings to varying degrees. After over a century of artifactual research, archaeologists and geologists have made great advances in understanding the prehistory of copper metalworking (Griffin, 1961; Libby, 1954; Martin, 1999). However, the specifics regarding the patterns of intensive metalworking in the Lake Superior region have remained elusive. In this dissertation I propose that environmental changes related to copper mining and annealing can be measured using sediments in nearby lakes to investigate the location, duration and magnitude of the prehistoric copper industry. I retrieved and analyzed sediment cores from seven lakes near ancient copper mines on the Keweenaw Peninsula and Isle Royale, Michigan.

Sorbed metals were extracted and measured from Holocene sediments in seven lakes from the Michigan Copper Districts located near ancient mine copper mines noted by Whittlesey (1862) and Gillman (1873). All five of the lakes analyzed on the Keweenaw Peninsula contained anomalous increases in sorbed lead and potassium that occur at varying times from 9600 to 5000 yr BP. Lead concentration were normalized to site specific background averages and reference metals that are found in high concentrations in the Portage Lake Volcanic bedrock to account for the relative importance in the processes affecting the flux of sorbed metals to the lake basin

(Boës et al., 2011; Weiss et al., 1999). All the sites record multiple anthropogenic perturbances in the past, except at Lake Medora which only extends back to ~7000 yr BP, and at Boston Lake which records one increase in sorbed Pb and K ~9200 yr BP. At Copper Falls Lake, Seneca Lake, and Lake Manganese, periods of Pb enrichments were recorded up to four times over several decadal to centennial periods occurring at each site. After 5000 yr BP, no Pb enrichments occur at any lake site analyzed on the Keweenaw Peninsula. Similarly, no increases in Pb are detected at the two lake sites (McCargoe Cove and Chickenbone Lake) analyzed on Isle Royale after 5000 yr BP until ~1860 AD. On Isle Royale, increases in Cu, in addition to Pb and K, related to copper mining on Minong Ridge are detected in the sediments of McCargoe Cove from ~6500 to 5400 yr BP, because McCargoe Cove receives drainage from ancient copper mines. At Chickenbone Lake no metal increases related to copper mining are detected in the prehistoric sediment record since ~10000 yr BP, likely because copper mining did not occur in the watershed of Chickenbone Lake. This is consistent with findings from the Keweenaw Peninsula, which indicate that emissions from ancient copper metalworking were localized.

The stable isotopes of N and C in organic matter sedimented in Copper Falls Lake and Boston Lake are used to infer paleoenvironmental context of mining on the Keweenaw Peninsula. Higher C/N and lower $\delta^{13}C$ are interpreted to reflect wetter conditions and enhanced carbon delivery from the watershed, whereas the reverse indicates drier conditions. The $\delta^{13}C$ and C/N records at Copper Falls Lake and Boston Lake, indicate drier conditions from ~10000 to 6500 yr BP, followed by relatively wet conditions from 6500 yr BP to present. This pattern is consistent with findings from other paleoclimate studies in the region (Booth, 2002; Brugam and Johnson, 1997). In addition, comparisons between $\delta^{13}C$ and sorbed Pb records from Copper Falls and Boston Lake suggest that landscape disturbances may have been associated with

copper mining at Copper Falls Lake ~5500 yr BP. However, the coincidence with climate change events detected at Elk Lake Minnesota (Smith et al., 2002) and other paleoclimate proxies (Kirby et al., 2002; Yu et al., 1997), raise the possibility that the $\delta^{13}C$ aberration may be related to other causes. Thus, additional proxy indicators are needed to test the landscape disturbance hypothesis.

In general, the findings from lake sediment from the Michigan Copper Districts suggest that emissions from copper mining (Martin, 1999) can be detected in lake sediments that are dated to a period prior to the emergence of agriculture in North America (Smith, 2011). The data presented here answers some of the primary questions raised by early researchers concerning the timing and location of the ancient mining period, as well as providing new insights into how the copper industry grew and declined through time. Notably, the advent of an intensive metalworking industry prior to agriculture contrasts with the birth of metalworking activities in many other regions of the world (Aldenderfer et al., 2008; Chiou-Peng, 2009; Radivojević et al., 2010), implying that these records could hold information regarding the emergence of higher social complexity in North America. The availability of prehistoric human proxy records from this region will refine our understanding of human-environmental change in the United States and transform our understanding of early copper metalworking in North America.

6.2 CAHOKIA

Sediments from Horseshoe Lake were analyzed over the last 1500 years to document landscape disturbances during the growth and decline of nearby Cahokia, the largest Mississippian-era (~1000 to 1400 AD) city in the United States. Previous sedimentological work studying human-environmental interaction at Horseshoe Lake focused on vegetation changes inferred from pollen, however no studies to date have investigated whether changes in the cycling of metals and nitrogen at Horseshoe Lake can be used to infer landscape disturbances. Here I analyze sorbed metals (Pb, Cu, K, Al) and nitrogen isotopes ($\delta^{15}N_{org}$) because they remain comparatively constant in the sediments of Horseshoe Lake in the absence of human activities and therefore are relatively insensitive to natural factors impacting the lake, such as flooding. Around 1150 AD, $\delta^{15}N_{org}$ values increase to ~4‰ followed by a distinct increase in sorbed aluminum, copper, and potassium concentrations that coincide with the construction of a copper workshop at Cahokia ~1200 AD and peak in human populations as inferred from the archeological record (i.e., Stirling and Moorehead Phases). This transition corresponds with the deposition of a ~20 cm thick gray layer between ~1150 to 1220 AD containing kaolinite, which we interpret to be the result of anthropogenic disturbances to the watershed, similar to the Maya Clay layer(s) found in lakes in Central America. Around 1220 AD, sorbed copper, potassium, and aluminum concentrations decline to background levels, followed by a decrease in $\delta^{15}N_{org}$ from ~1300 to 1400 AD. These data suggests that sorbed metals and $\delta^{15}N_{org}$ analyzed in lake sediments from Horseshoe Lake can be used to inform our understanding of the timing, magnitude, and processes by which human activities associated with Cahokia impacted the environment.

6.3 POTENTIAL FUTURE RESEARCH

The advent of the new organic proxies in lake sediment holds promise for investigating human-related impacts to lakes. For example, D'Anjou et al. (2012) measured fecal sterols, such as coprostanol (and its epimer epicoprostanol) and 5β-stigmastanol (and 5β-epistigmastanol) in lake sediment from Norway, which they interpret to result from human and animal feces washing into the lake. Fecal sterols and their use as a proxy for human activities will face problems, but they appear to be advantageous with respect to conventional proxies because they are directly linked to human activity. In contrast, other proxies that have been traditionally used to understand human disturbances to lakes, such a magnetic susceptibility, pollen, and charcoal, can be influenced by a multitude of natural factors that complicate their use as evidence for anthropogenic activities (Carson et al., 2014; D'Anjou et al., 2012). Other novel organic proxies, such a levoglucosan (Kehrwald et al., 2012) and polycyclic aromatic hydrocarbons (PAHs) (Denis et al., 2012) also hold potential for understanding biomass burning related to human activity, because these molecular compounds are produced directly from the burning of biomass, such as wood. Traditionally, charcoal >63 μm in size that is isolated and counted in sediments has been used a proxy for fires around lakes, however the majority of particulates from wood smoke emissions are <63 μm (Kleeman et al., 1999). Levoglucosan and PAHs, in addition to sorbed potassium as presented in this dissertation, may provide a means to detect fine particulates emitted from burning biomass, which could provide an alternative to macroscopic

charcoal analysis. In time, sorbed potassium or levoglucosan could potentially be used to calculate carbon emissions from prehistoric societies, which could eventually aid in identifying sources of the anomalous increase in carbon dioxide and methane concentrations detected in Dome C ice core from Antarctica in the middle Holocene (Ruddiman, 2003; Ruddiman et al., 2011). Taking into account both natural and human-related factors when interpreting the paleo-records will lead to a more comprehensive view of global change over the Holocene, which may eventually help to explain the some of the underlying causes of environmental change detected during this time.

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